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INDUSTRIAL AND  
MANUFACTURING CHEMISTRY

*Part I. ORGANIC*



UNIFORM WITH THIS VOLUME



PART II. INORGANIC  
*IN TWO VOLUMES*

*Sixth Edition Revised by*

W. FRANCIS, M.S.C., PH.D., F.R.I.C., F.S.C., F.INST.F.

About 500 pages each, with numerous illustrations



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# INDUSTRIAL AND MANUFACTURING CHEMISTRY

## PART I. ORGANIC

### *A PRACTICAL TREATISE*

BY

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Seventh Edition Revised

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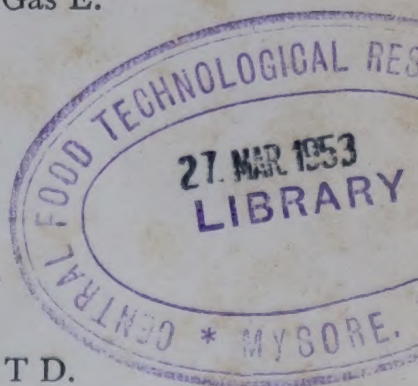
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## PREFACE TO FIRST EDITION

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THIS book is a treatise on the applications of Organic Chemistry to the arts and manufactures. It embraces both British and American practice, and affords, so far as is ascertainable in view of the many secret processes employed, thoroughly up-to-date information regarding the various branches of chemical industry and of manufactures having a chemical basis.

The editor's aim has been to cover the whole range of subjects with which the industrial chemist and manufacturer are usually concerned, and the book will serve either as a text-book or as a work of reference; it is intended to meet the requirements of all business and practical men interested in chemical processes, of manufacturers, consulting chemists, chemical engineers, patent workers, inventors, technical lawyers, students in technical institutions, lecturers on technology, fire insurance inspectors, and others.

Statistics, so important from a commercial standpoint, are made a feature of the work.

Particular pains have been taken to incorporate not only the main industries but also minor industries and new and out-of-the-way processes and products, the details of which are usually known to and obtainable by only a limited circle; moreover, these minor industries have potential importance as the germs of future great industries, and frequently, too, as affording, through absence of competition, profits far greater than those of fully developed trades. A striking example of this is afforded by artificial silk, which so took the market by storm (on account of its extreme brilliance) that for a time its price actually exceeded that of the real article.

The profitable utilisation of by-products—a matter of great importance to many manufacturers—has received special consideration.

Patent specifications are usually the first and often the only information appearing in regard to a technical process, and it is therefore unnecessary to apologise for the large number of recent



patents referred to in the text. Commercially many of them are unremunerative, yet they often contain useful ideas.

Matters calling for industrial research have been specially emphasised by the editor; for he has recognised that the subject of chemical industry is not only one which is full of problems whose solution demands the highest technical skill, but also one that holds out prizes of very great value to the scientific worker. For example, great fortunes lie in the discovery of economical processes for converting heavy mineral oil into light motor spirit, for the synthetic production of rubber, or for the proper utilisation of old leather for glue and gelatine manufacture; while the most far-reaching changes in the social and economic life of civilised nations have been made by the discovery of chemicals such as nitro-explosives, vulcanised rubber, synthetic dyes and drugs, technical alcohol, motor spirit, alkalis, glasses, metals, and artificial manures.

Much of the information in this volume is published in book form for the first time, and many of the descriptions of new processes and modern plant have been privately supplied through the courtesy of industrial chemists and of leading firms of Europe and America.

Full literary references are prefixed to each article, so that the reader may have before him at once the main authorities of all countries. Indeed, the editor ventures to think that the account of literature relating to chemical technology in its organic branches is the most complete ever published in English, and to hope that it will accordingly prove indispensable to the manufacturing or consulting chemist, the student, and the business man; for these often experience extreme difficulty in ascertaining where to find quickly some special piece of information lying outside the confines of the main industries.

The index has, therefore, been made as complete as possible, and numerous cross references are given.

The development of industrial chemistry, and the variety and comprehensiveness of its applications, has proceeded, during the past few years, at a rate so bewildering, and has taken such curious and unexpected turns, that the days are now past when one man, however well qualified, could keep abreast of recent advances in the different branches. Consequently, the editor has been fortunate in securing the co-operation of a number of experts as contributors on their special subjects: their names and attainments, enumerated on the title-page, and, more specifically, in



the List of Contents, are a guarantee that the minutest care has been exercised to ensure accurate descriptions of the industries concerned, and to these gentlemen the editor owes a considerable debt of gratitude.

It is impossible to thank in detail all those who have supplied information, or who have given help in subjects in which they have specialised. Nevertheless the editor cannot forego expressing his indebtedness to—Dr H. J. S. Sand, of Nottingham, for expert technical information; Dr G. Druce Landier, of London, for advice on certain technical problems; Mr C. Ainsworth Mitchell, B.A., F.I.C., for information on Vinegar Manufacture and for suggestions; Dr Newton Friend for help and advice in preparing many sections; Mr Geo. Stade, technical chemist. Berlin, for information on Continental molasses distilleries; Mr Geo. Clough, B.Sc., for material assistance in many ways; Mr J. Louis Foucar, B.Sc., for expert advice on the Coal-Gas and Coal-Tar Product Industry; Mr Dewar, F.I.C., for information on Linoleum Cements; Mr Paul Arup for information on Margarine; Mr Ernest Dancaster, B.Sc., for information on the Turpentine Substitutes and on the Graphitic and Grey Paints used by certain engineering companies; Mr J. B. Cotton for help.

Among other gentlemen who have helped are—Mr W. H. Stephens, A.R.C.S.; Mr A. J. Carrier, B.Sc.; Mr T. Beacall, B.A.; Mr G. M. Painter, B.Sc.; Mr Milsom, B.Sc.; Dr A. Slator; Mr J. W. Barker, A.R.C.S., B.Sc.; Mr F. Allen; Mr J. E. Mason; and Mr W. F. F. Shearcroft. Many of the great chemical firms have supplied full details of their more important patents, and even drawings of the plant used in carrying out certain of their manufactures. To all of these the editor returns his best thanks.

Although every care has been taken in the production of this work, yet, in view of the mass of detail involved, it is impossible that all errors have been eliminated, or that in every case the best processes have been described. The editor will therefore be grateful if industrial chemists, manufacturers, and other practical men will kindly inform him of any erroneous statements, or will call his attention to any serious omissions. Suggestions for increasing the utility of the work will be especially welcome.

## PREFACE TO SEVENTH EDITION

THE organic division of our modern chemical industry is one of the most far reaching—indeed, it may be said to enter into the everyday life of us all.

When the writer first read the sixth edition before beginning his task of revision, he marvelled that such a wide field had been covered in so little space. Since 1922 the field has become infinitely wider; the plastics industry has grown from one little known to one of the largest; the petroleum refining industry has become strategic, and many new and marvellous drugs have come into being.

In this edition the following old sections have been *completely rewritten*: "Mineral Oils and Lubricants" with the "Cracking and Pyrogenesis of Petroleum and Mineral Oils" now appearing as "The Petroleum Refining Industry" by E. S. Sellers, M.Sc.(Lond.), A.M.I.Chem.E., F.Inst.Pet.; "Condensed Milk and Milk Powders" by the Editor; "The Fatty Acid Industry" (now separated from the section on Candles) by Mr I. McArthur; "The Illuminating Gas Industry," rewritten as "The Fuel Gas Industry" by P. C. Bishop, B.Sc., A.R.I.C., Assoc.M.Inst.Gas E.; "The Industry of Coal Tar Products," rewritten as "The Coal Tar Industry" by R. A. Jones, B.Sc., A.R.I.C.

The section entitled "The Modern Explosives Industry" has been omitted from this edition on account of difficulty in obtaining modern data. It has been replaced by a section on "The Plastics Industry." The latter section has been considerably curtailed by reason of the space available.

The following sections have been thoroughly revised: "The Sugar Industry" by J. L. Fergus, A.H.-W.C., A.R.I.C.; "The Rubber Industry" by D. E. Partington, A.I.R.I., and "The Industry of Modern Synthetic Drugs" by the Editor.

Other sections have been brought up to date where possible by additional material replacing obsolete material, or more often by additions at the end of the sections. In this case they have become an historical review of the subject and do not claim to be of use to the expert. Indeed the whole treatise is admirably suited and recommended to those experts who wish to enlarge on their knowledge of subjects other than their own. The fact that twenty-four subjects are dealt with in less than seven hundred pages naturally reduces the scope available.

Besides the above, this book is thoroughly recommended to sixth-form and university students deciding on their future career, and to all who wish to know more of British Industry.

In conclusion the Editor would like to express his grateful thanks to his collaborators in the onerous task of revision and to numerous firms who have kindly supplied illustrations. Due acknowledgment to these firms has been made in the text.

E. I. C.



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Originally written by G. MARTIN, Ph.D., D.Sc.

Revised by E. I. COOKE, M.A., B.Sc., A.R.I.C.

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## SECTION I

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# The Oil, Fat, Varnish, and Soap Industry





# THE OIL, FAT, VARNISH, AND SOAP INDUSTRY

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## I.—GENERAL NATURE OF OILS, FATS, AND WAXES

By the late C. AINSWORTH MITCHELL, B.A., F.R.I.C.

**Nature of Oils.**—The substances popularly known as “oils” fall naturally into the three groups—mineral, essential, and fatty oils.

To the first group belong the petroleum derivatives, consisting, in the main, of mixtures of various hydrocarbons, which, since they boil at different temperatures, may be separated by distillation into fractions such as naphtha, kerosene, heavy lubricating oils, and paraffin wax.

Essential oils, which constitute the second group, are volatile substances which occur in different parts of plants. For the most part they are mobile liquids, lighter than water, and as a rule are completely volatile without decomposition. Exceptionally, as in the case of oil of wintergreen which is fairly pure methyl salicylate, they do not consist mainly of a single compound, but usually they are composed of mixtures of various chemical compounds, such as hydrocarbons, aldehydes, and alcohols. The characteristic odour or flavour of an essential oil is usually centred in one or more of these constituents, and an estimation of the proportion of these substances affords a means of judging of the value of a given oil.

Fatty oils, which form the third group, are deposited in the adipose tissue of animals, or in the oil cells of seeds or other parts of plants, occurring in the form of minute globules enclosed within a thin skin. Chemically, they consist of compounds of an alcohol such as glycerol with one or more fatty acids. In these glycerides the three bonds of the glycerol may be in combination with the same fatty acids (*e.g.*, tristearin); or two bonds may be in combination with one fatty acid and the third with another one (*e.g.*, dipalmitostearin); or all three bonds may be combined with different fatty acids (*e.g.*, oleo-palmito-stearin). Mixed glycerides of the two latter types have been discovered in natural fats.

The properties of the fatty acids isolated from fats by means of saponification afford valuable analytical evidence of the nature of the oils whence they are derived.

Waxes differ from fats, properly so-called, in having the fatty acids combined with an alcohol other than glycerol. Thus sperm oil, regarded from a chemical point of view, is as much a wax as the typical product, beeswax; whereas Japan wax, so-called from its wax-like appearance, is in reality not a wax at all, but a true glyceride.

## II.—THE PETROLEUM REFINING INDUSTRY

BY E. S. SELLERS, M.Sc. (London), A.M.I.Chem.E., F.Inst.Pet.,  
Lecturer in Petroleum Technology, Manchester Municipal  
College of Technology.

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**Crude Petroleum.**—Crude petroleum is essentially a mixture of hydrocarbons, together with small amounts of oxygen, nitrogen, and sulphur compounds.

The ultimate analysis of most crude oils gives the following composition:—

Carbon,	83-87 per cent.
Hydrogen,	11-14 „
Oxygen	} 0-4 „
Nitrogen	
Sulphur	

The actual chemical constituents of crude petroleum have been divided into three main groups: paraffins, naphthenes, and aromatic compounds. The paraffins may be either straight or branched chain, and range from methane up to the high molecular weight paraffin waxes.

Naphthenes, or cycloparaffins, are mainly derivatives of cyclopentane, and cyclohexane, with varying length of paraffin side chains.

Compounds have been isolated containing two naphthene rings, corresponding to hydrogenated naphthalene derivatives.

Aromatic compounds, that is compounds whose molecules contain a benzene, naphthalene or anthracene, etc., nucleus, are present in most crude oils. Benzene and toluene can be extracted in considerable quantity from Borneo crude, and



aromatic compounds with paraffin side chains occur in all other crudes to a greater or lesser extent.

A good empirical method for estimating the proportion in the oil of aromatic rings, naphthene rings, and paraffin chains has been described by Vlugter, Waterman and Van Weston,<sup>(1)</sup> and is now in general use. This method, which is applicable to petroleum fractions is based on the molecular weight, aniline point and the Lorentz-Lorenz Specific Refractivity.

In a paper published in 1940,<sup>(2)</sup> H. M. Smith proposed a method of classification which he called "Correlation Index." The basis of this is as follows. If the specific gravities of the pure paraffins are plotted against the reciprocal of their boiling-points in degrees Kelvin, we obtain a linear relationship, as shown in Fig. 1. The line parallel to this and passing through the point for benzene is then drawn. The sample of crude oil under test is distilled into successive fractions of about 5 per cent., and the reciprocal of the average boiling-point plotted against the specific gravity of the fraction.

From the resulting curve it is possible to predict the properties of all the distillates, bearing in mind the "pour point" or setting temperature of the fraction. Fig. 1 shows the curves drawn for a Middle East and a Texas Gulf Coastal crude respectively. The Correlation Index represented by any point on the curve is given by the ratio of the distance of the point from the paraffin line to the distance between the paraffin and benzene lines. Smith suggests the fractions with index values from 0 to 15 are almost certain to be predominately paraffinic; values from 15 to 50 indicate naphthenes or different mixtures of paraffins, naphthenes and aromatics; and values above 50 indicate that aromatic rings probably predominate. The addition of paraffin side chains to aromatic nucleus, such as naphthalene, decreases the index value, and if the side chains are long enough the molecule begins to assume paraffinic characteristics.

It is quite possible for two fractions of widely different characteristics to have the same correlation index. For instance, referring again to Fig. 1, the Gulf Coastal distillate, which is largely naphthenic, has at one point the same value as the "Arabian" distillate. The low pour point of the former shows that it is largely naphthenic, while the high pour point of the latter suggests that the mixture is one of paraffins and aromatics.

**Classification of Crude Oils.**—The old classification of paraffin, asphalt, or "mixed" base has now been abandoned, being replaced by the U.S. Bureau of Mines Classification.<sup>(3)</sup> In this method, two key fractions are distilled from the crude oil, the first having a boiling range from 250° C. to 275° C. at 760 mm. absolute pressure, and the second having a boiling range between 275° C. and 300° C. at 40 mm. absolute pressure.

According to the specific gravity of the fraction, the oil is then classed as paraffin, naphthene or intermediate according to Table I.

It will be seen that there are nine possible descriptions to describe the "base" of any crude oil, sufficient to leave no room for misunderstanding.

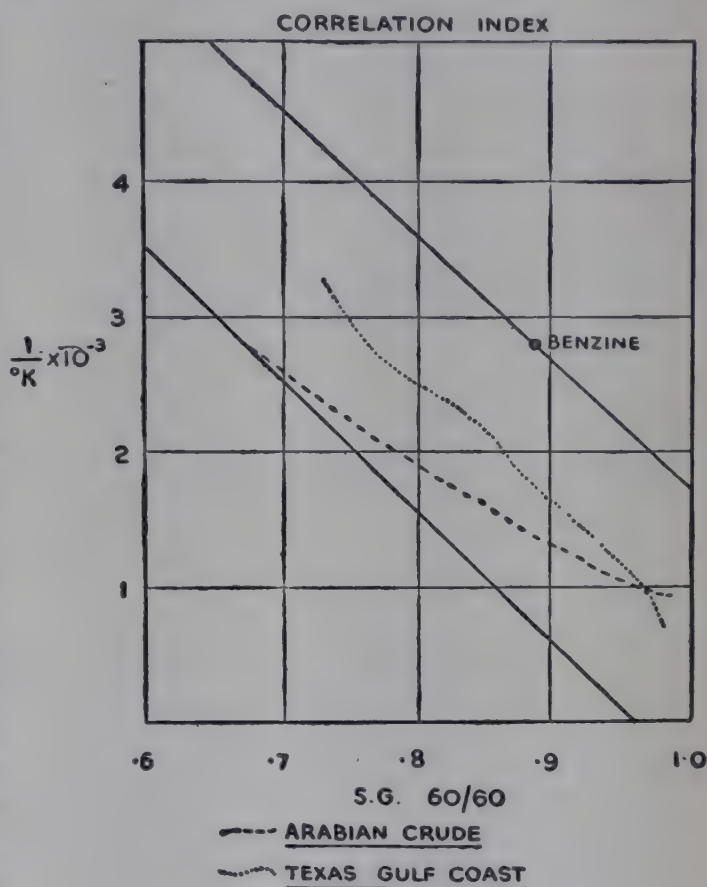


FIG. 1.

TABLE I

No.	Gravity of Key Fraction 1. Specific Gravity 60/60° F.	Gravity of Key Fraction 2. Specific Gravity 60/60° F.	Base of Crude.	
			Light Fraction.	Heavy Fraction.
1	0.8251 or lighter	0.8762 or lighter	Paraffin	Paraffin
2	"	0.8767 to 0.9334	"	Intermediate
3	"	0.9340 or heavier	"	Naphthene
4	0.8256 to 0.8597	0.8762 or lighter	Intermediate	Paraffin
5	"	0.8767 to 0.9334	"	Intermediate
6	"	0.9340 or heavier	"	Naphthene
7	0.8602 or heavier	"	Naphthene	"
8	"	0.8767 to 0.9334	"	Intermediate
9	"	0.8762 or lighter	"	Paraffin

Another relationship which has been used to a considerable extent in correlating the properties of hydrocarbons is the so-called "Characterisation Factor" K, proposed by Watson and Nelson.<sup>(4)</sup> This is given by

$$K = \frac{\sqrt[3]{R}}{G}$$

where R is the average boiling-point of the fraction in degrees Rankin ( $^{\circ}$  Fahrenheit + 460), and G is the specific gravity. Characterisation factors for various typical oils are:

TABLE II

Type of Oil.	Base.	S.G. at 60° F.	K.
Pennsylvanian distillate . . .	Paraffin	.860	12.5
Middle East Arabian gas oil . .	Paraffin-Intermediate	.859	11.9
Gulf Coastal, gas oil . . .	Naphthene-Intermediate	.868	11.2
Gulf Coastal, lubricating oil }		.926	11.5
Gulf Coastal—Solvent extract .		.960	10.7

Much useful data is available correlating physical and chemical relationships, such as molecular weight, specific gravity, viscosity, specific heat and so on, with "Characterisation factor."<sup>(5)</sup>

**Sulphur, Oxygen and Nitrogen Compounds.**—Sulphur occurs to some extent in all petroleum distillates in one of the following forms:—<sup>(6)</sup>

1. Free sulphur.
2. Hydrogen sulphide.
3. Organic sulphur compounds.
  - (a) Mercaptans or alkyl hydro sulphides,  $(C_nH_{2n+1}SH)$ .
  - (b) Alkyl sulphides,  $(C_nH_{2n+1})_2S$ .
  - (c) Alkyl sulphates,  $(C_nH_{2n+1})_2SO_4$ .
  - (d) Sulphones,  $C_nH_{2n}SO_2$ .
  - (e) Thiophene,  $C_4H_4S$  and its homologues.
  - (f) Thiophanes,  $C_nH_{2n}S$ .

Oxygen is present in small amounts, in various forms, such as

- (1) Naphthenic acids— $C_nH_{2n-1}COOH$ .
- (2) Phenols.
- (3) Asphaltic or resinous bodies.



Nitrogen compounds are also present to a small extent, and it has been suggested that these compounds consist chiefly of alkylated quinolines or isoquinolines.

**Petroleum Products—Utilisation, and Criteria of Quality.**—Fig. 2 shows a distillation curve for a typical crude oil, and the division and origin of the various petroleum products obtained is easily seen.

Before describing the many and complex manufacturing processes, it is necessary to consider the desirable quantities of the whole range of petroleum products, which range from natural gas to hard asphalt.

(1) **Petroleum Gas.**—A typical analysis of a "wet" gas is:

Methane	.	.	87.04 per cent.
Ethane	.	.	4.13 "
Propane	.	.	2.56 "
Butane	.	.	2.00 "
Pentane and heavier	.	.	3.42 "
CO <sub>2</sub>	.	.	1.11 "

Natural gas is used as a fuel; about one-third of the domestic gas consumed in the U.S.A. is "natural." Gas is used for the production of hydrogen (by heating with steam in presence of a suitable catalyst at 900° C.), and for the production of Carbon black. Liquefied propane is used for welding, and liquefied butane as "Calor" Gas for domestic use.

(2) **Motor Fuels: Gasoline.**—

Gasoline, or petrol, is the name given to the mixture of hydrocarbons, the boiling range of which is from 35° C. to about 190° C. This mixture is usually a blend of "straight run" spirit, *i.e.*, distilled from the crude oil, and "cracked spirit," manufactured from other fractions by the special processes described later.

Improvements in the quality of motor fuel have been concurrent with the development of the internal combustion engine for motor cars and aircraft.

The characteristics demanded in a motor fuel are:

- (1) Volatility sufficiently high to give easy starting.
- (2) Absence of high boiling fractions which may not be vaporised and which will cause crank case dilution.
- (3) Vapour pressure not too high so as to avoid vapour lock in the feed pipe.
- (4) Low sulphur content to avoid corrosion.
- (5) Stability in storage to avoid "gum" formation.
- (6) Good anti-knock properties, *i.e.*, ability to use the fuel with a high compression ratio engine.

Numbers 1, 2 and 3 may be specified in the boiling range of the gasoline, together with the Reid Vapour Pressure test. Fig. 3 shows the boiling range of aviation, No. 1, and No. 3 motor spirits.

Number 4. Sulphur content should not exceed .03 per cent.

Number 6. This is, after volatility, the most important characteristic, because it directly affects the design and performance of internal combustion engines.

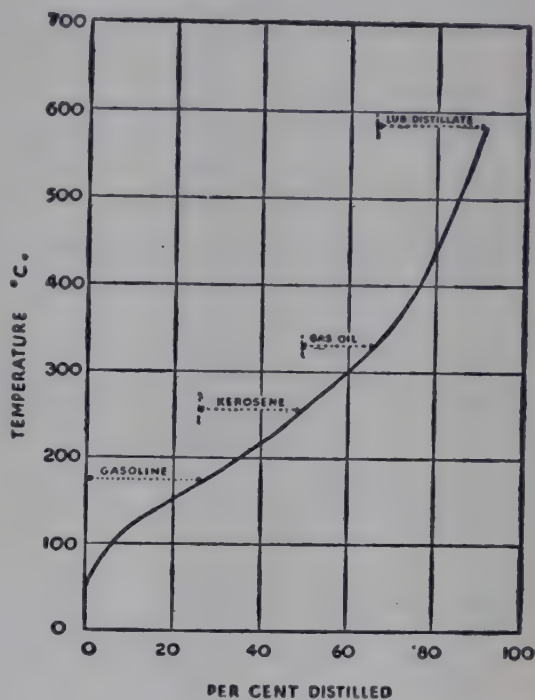


FIG. 2.

The theoretical efficiency,  $E$ , of an engine operating in the constant volume cycle is given by

$$E = 1 - \left(\frac{1}{R}\right)^{\gamma-1}$$

when  $R$  = compression ratio and, in practice,  $\gamma$  is almost 1.296. Fig. 4 shows the effect of compression ratio on efficiency, so that the higher the compression ratio the more efficient the engine.

If the compression ratio is increased too much, the engine runs with a dis-

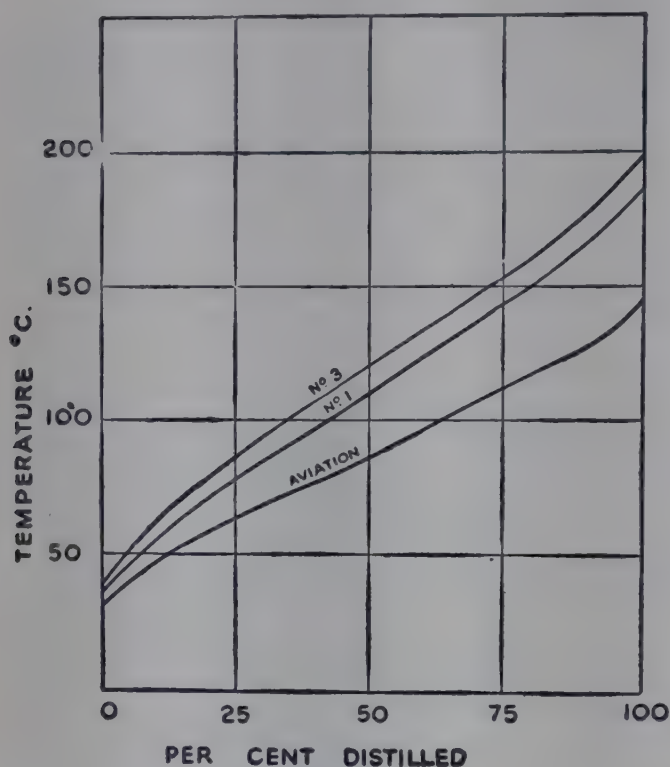


FIG. 3.

concerting "knock," with loss of power. "Knock" is a characteristic of the chemical constitution of the fuel. In general, aromatic compounds are better than naphthenes or olefines which, in turn, are better than the straight chain paraffins. The addition to the fuel of small amounts of certain substances such as tetra-ethyl lead has the effect of suppressing "knock." Isoparaffins have good anti-knock qualities, and *isooctane*, 2,2,4-trimethylpentane, has been adopted as a primary standard for the measurement of anti-knock properties of other fuels. This is considered to have a rating of 100 and, at the other end of the scale, *n*-heptane has a rating of zero. The "knock rating" of a motor fuel is obtained by running in a standard engine under standard conditions a comparison test between the fuel under review and a blend of *isooctane* and *n*-heptane. The mixture strength is

adjusted so as to give maximum knock at a certain compression ratio with the fuel sample, and the blend of *isooctane* and *n*-heptane which gives identical results is then determined. The octane rating of the fuel is equal to the percentage of *isooctane* in the matching blend.<sup>(7)</sup>

The octane rating of motor gasoline is 70–80, while that for aviation gasoline is 100 for most modern engines.

**Special Boiling-Point Fractions.**—Light fractions with narrow boiling ranges are distilled from the crude oil and are used as solvents. The very light solvents, with final boiling-points of up to about 80° C. are known by the name of "Petroleum Ethers." Those which boil up to about 160° C. are referred to as "S.B.P.s" (Special Boiling-Point Spirits). The fraction boiling from 150° C. to 200° C. is known as "White Spirit," and "Rubber Solvent" is a fraction with a boiling range from 100° C. to 160° C.

**Kerosenes.**—Kerosene is the fraction with a boiling range from about 150° C. to about 275° C. There are two main uses for kerosene: (1) as a burning oil in lamps, and (2) as a fuel for internal combustion engines—this fuel is known as "Power Kerosene" or "Tractor Vaporising Oil." Kerosene is also used with success as a fuel for jet engines and gas turbines.

The characteristic requirements are:—



(1) **Burning Oil.**—This must have a minimum closed flash point of  $73^{\circ}$  F., and should burn with a clear white flame. It should have no objectionable odour and as low a sulphur content as possible. The best burning oils are those made from the distillates of paraffin base crude, or by solvent extraction from the distillates of other crude oils.

(2) **Power Kerosene.**—This should have a relatively high flash point ( $90^{\circ}$  F.), and a minimum of about 40 per cent. distilling at  $200^{\circ}$  C.

(3) **Gas Turbine Fuels.**—It has been suggested that gas turbines are omnivorous with regard to fuels, but certainly so far as aircraft engines are concerned, there are serious limitations to what can be used as fuel. For a variety of practical reasons, a kerosene with a boiling range of  $65^{\circ}$  to  $300^{\circ}$  C. is preferred.<sup>(8)</sup> Properties most desirable in aviation kerosenes are:

1. Low freezing point.
2. Low water tolerance.
3. Low viscosity.
4. High calorific value.
5. Reasonably high volatility.

**Diesel Fuel—Gas Oils.**—Reference has already been made to the increased efficiency that increased compression ratio gives to the internal combustion engine.

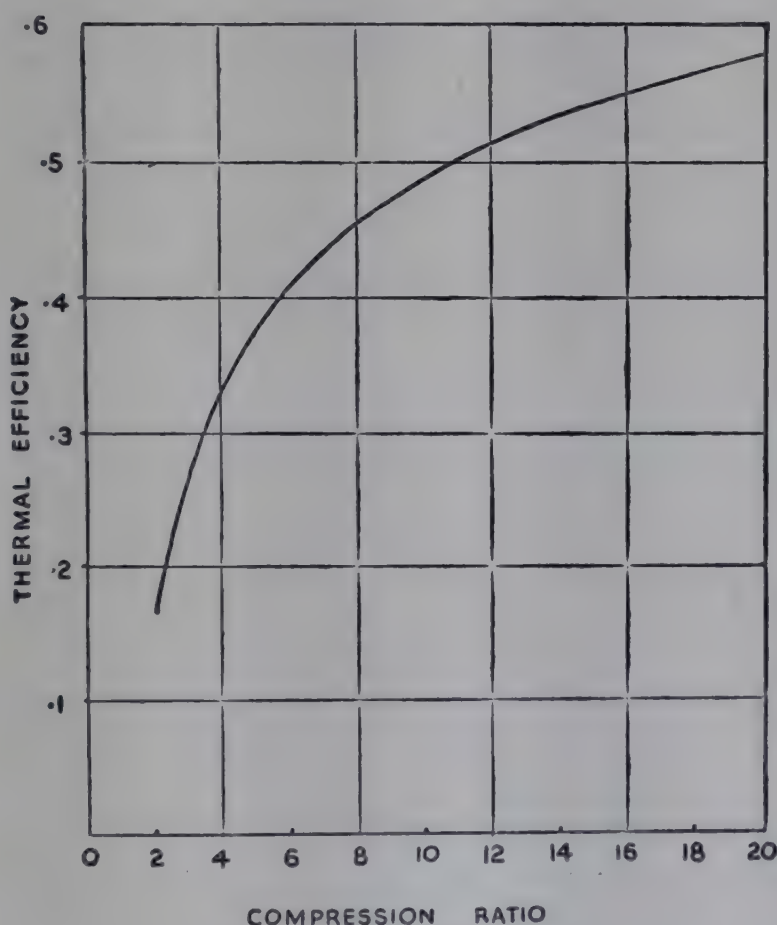


FIG. 4.

The petrol engine operates at a compression ratio of about 6 to 1, and the compression ignition engine at about 14 to 1. Consequently there is a great demand for high speed light-weight Diesel engines in road vehicles. The fuel for these engines must have certain characteristics.

- (1) The closed flash point must exceed  $150^{\circ}$  F. for safety reasons.
- (2) The viscosity should not exceed 45 Redwood seconds at  $100^{\circ}$  F. This

is important because of the necessity of obtaining good atomisation when the fuel is injected into the cylinder.

(3) The fuel should ignite and burn in the cylinder with as little delay as possible. Paraffin base oils of distillation range of about  $195^{\circ}$  to  $300^{\circ}$  C. make the best high speed Diesel fuels. A criterion of quality known as "Diesel Index" is used in specifications. The "Diesel Index" is given by

$$\frac{\text{Gravity at } 60^{\circ} \text{ F. in } ^{\circ} \text{ A.P.I.} \times \text{Aniline Point in } ^{\circ} \text{ F.}}{100}$$

$$^{\circ} \text{ A.P.I.} = \frac{141.5}{\text{S.G.}} - 131.5.$$

Paraffin base oils have a lower gravity and a higher aniline point than naphthenes or aromatics, so have a higher Diesel index.

For low speed Diesels, such as are used for marine propulsion, it is customary to use a heavier fuel.

Gas oil, used for carburetting in gas manufacture, has approximately the same boiling range as the high speed Diesel fuel, and should have a low sulphur content and as high a hydrogen:carbon ratio as possible. Paraffin base oils are preferred, and cracked gas oil is quite admissible. An evaluation factor, proposed by Schlupfer,<sup>(9)</sup> is  $\frac{KH}{G}$ . Where K is the average boiling-point of the oil under 10 mm. pressure

H is the hydrogen content.

G is the specific gravity.

Gas oil is also used as an absorbent in benzol recovery plants.

**Oil Fuel.**—Oil is used for a very large number of heating purposes and has many advantages over solid fuels. In order to secure the most efficient utilisation, these are the factors which must be considered.

(1) The correct conditions for combustion. This includes a properly designed atomising burner, and careful regulation of the supply, temperature and mixing of air.

(2) A combustion chamber of the right shape and dimensions.

The two characteristics of the fuel itself which are considered most important are calorific value and viscosity. An empirical relationship for the value of the gross calorific value of a fuel is

$$22,320 - 3780G^2 \text{ B.T.U per lb.}$$

where G is the specific gravity. From this it is apparent that the lower gravity fuels have the higher calorific value per pound, though as fuel oil is usually purchased on a volume basis, it is important to note that a gallon of high gravity fuel may have a greater total heating value than a gallon of lighter fuel.

The importance of viscosity is once again connected with the ease and efficiency of atomisation at the burner tip. Fuel oils may be anything from light distillates of the gas oil type to heavy residues obtained in the distillation of crude oil. The former have low enough viscosities to be satisfactorily atomised without pre-heating, but residue fuels must be heated to be handled satisfactorily. For instance, a heavy marine fuel may have to be heated to  $200^{\circ}$  F. in order to secure good atomisation at the burner.

**Lubricating Oils.**—"Lubrication" consists of the maintenance of a fluid film between two rubbing surfaces. The importance of viscosity in this connection has long been recognised. Osborne Reynolds,<sup>(10)</sup> in 1886, enunciated the mathematical theory of film lubrication, and it was known that film lubrication conditions depended on the viscosity of the oil and the relative speed and load between the two bearing surfaces.

Reference to Fig. 5 will indicate why low viscosity oils are in use for high speeds and light bearing pressures, such as in the lubrication of spindles in the



cotton spinning industry, and why high viscosity oils are used in low speeds and high loading such as obtain with gears.

In the internal combustion engine there is the additional factor of high temperature. Consequently emphasis is placed on a lubricating oil having (1) stability at high temperature, and (2) an adequate viscosity at the high temperature, so that the film lubrication conditions are maintained.

Stability at high temperatures is usually measured by the British Air Ministry Oxidation Test (Specification DTD 109). In this test, the "Carbon Residue" of the oil, *i.e.*, the amount of carbon left after pyrolysis of an oil under specified conditions is determined,<sup>(11)</sup> before and after oxidation. Viscosities before and

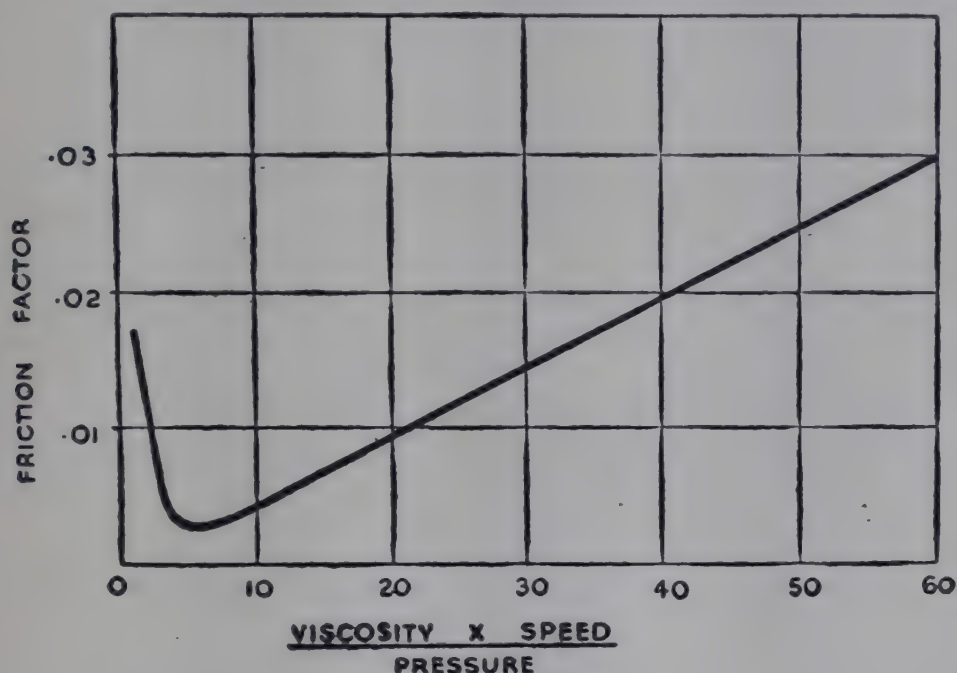


FIG. 5.

after oxidation are also compared. According to the specification, the viscosity should not increase to more than twice its original value, nor the carbon residue increase by more than 1 per cent.

Viscosity/temperature relationships are measured according to a scale known as "Viscosity Index" (V.I.).

All oils decrease in viscosity when their temperatures are raised, and it is desirable for internal combustion engine lubrication to select an oil which will decrease in viscosity as little as possible on heating. This ensures adequate viscosity for high temperature lubrication, and, at the same time, the viscosity when cold is not too high to prevent easy starting of the engine. The viscosity index scale was suggested by Dean and, Davis,<sup>(12)</sup> and is a function of the ratio of the viscosity at 100° F. to that at 210° F. for two reference oils and an unknown oil whose V.I. is to be measured. The two reference oils chosen were a Pennsylvania paraffin base oil with good viscosity/temperature characteristics, and an oil obtained from a Gulf Coast naphthene base crude with extremely poor characteristics. If the oil under consideration has a viscosity of  $U$  Saybolt seconds at 100° F. and  $V$  Saybolt seconds at 210° F., and a Pennsylvanian oil which has a viscosity of  $H$  seconds at 100° F. has a viscosity of  $V$  seconds at 210° F., and a Gulf Coastal which has a viscosity of  $n$  seconds at 100° F. and  $V$  seconds at 210° F.

$$\text{Viscosity index} = \frac{\frac{L}{\bar{V}} - \frac{U}{\bar{V}}}{\frac{L}{\bar{V}} - \frac{H}{\bar{V}}} \times 100 = \frac{L - U}{L - H} \times 100.$$

It is obvious that the Gulf Coast oils would have a V.I. of 0 and a Pennsylvanian oil a V.I. of 100. Charts have been worked out so that the V.I. can be calculated directly from the viscosities at 100° F. and 210° F., determined on the oil under test.

It should be noted that although reference has been made to "paraffin base" lubricating oils, it does not follow that the oil consists of mixtures of paraffin hydrocarbons. Indeed, this cannot be so, because the paraffins of this molecular wt. (350–550) are solid.

Waterman analyses of a "paraffin base" and a "naphthene base" are compared below.

	<i>Paraffin base.</i>	<i>Naphthene base.</i>
Aromatic rings .	8 per cent.	32 per cent.
Naphthene rings .	15 „	29 „
Paraffin chains .	77 „	39 „

It is probable that length of the side chain on a naphthene or aromatic nucleus is the deciding factor in the viscosity index characteristics of an oil.

Other lubricating oils, such as those intended for steam turbine lubrication, must resist any tendency towards emulsification. This is tested by blowing steam into 20 mls. of the oil contained in a tube in a water bath at 25° C., until the total volume is 40 mls. The tube is then transferred to a second water bath at 94° C., and the time taken for the oil to separate is noted. This should not exceed 120 seconds.

**Electrical and Insulating Oils.**—The most important of these is "Transformer Oil." Petroleum oils have been employed as liquid dielectrics for a very long time, and their purpose is two-fold, insulation and heat conduction. Immersion of a device such as a transformer in a liquid insulating medium, allows distances between parts to be decreased, and the whole assembly may be immersed in a tank of oil, which protects it electrically from surrounding objects. The heat conduction factor is taken care of by an oil of low viscosity, which allows easy convection with consequent dissipation of the heat caused by local high temperatures. The qualities desired in oils for transformers and switchgear may be listed as:

1. High dielectric strength.
2. Minimum sulphur, with absence of acidity and alkalinity.
3. Low viscosity to ensure rapid convection, together with ability to flow at very low temperatures.
4. No tendency to form emulsions with water.
5. Good resistance to oxidation in service as measured by sludge formation, or to carbon formation should an arc be struck.
6. Low volatility and as high a flash point as possible.

Transformer oil must comply with the British Standards Specification No. 148 of 1933.

Most transformer oils are manufactured from naphthene base crudes, the fraction boiling between 310° C. and 430° C., of molecular weight about 320 being taken as the starting point in the manufacturing process.

Petroleum oils, either alone or mixed with rosin, are used as insulating material in cables. An oil of high viscosity, about 150 centistokes at 140° F., is used. This is made by the refining of a high boiling-point distillate, and, on the whole, a naphthene-intermediate base oil is preferred.

**White Oils.**—The most familiar example of a white oil is medicinal liquid paraffin. These completely colourless oils are made by treating an appropriate distillate or solvent extracted distillate with fuming sulphuric acid.

Depending on viscosity, white oils are used as non-staining lubricants, transformer oil (British Standard Specification for A30), non-carcinogenic spindle oils, or for medicinal purposes.



**Petroleum Waxes.**—The waxy materials derived from petroleum are classified into three groups.<sup>(13)</sup>

- (1) The paraffin wax group.
- (2) The petrolatum group.
- (3) The petroleum ceresin group.

The waxes in the first group have a pronounced crystalline structure and are derived almost wholly from the distillate fractions from which lubricating oil is manufactured, by a "dewaxing" process described later. Paraffin waxes which, when freed of oil and suitably refined are white, find application chiefly in candle manufacture, waxed paper and cartons, and polishes.

Paraffin wax is usually marketed according to a melting-point specification.

The waxes of the petrolatum group are derived mainly from the waxy residues from the distillation of certain crude oils. Their crystalline structure is much less well defined than that of paraffin wax. They are subdivided on the basis of oil content into two sections, (1) petrolatum wax, which is substantially oil free, and is a plastic solid, and (2) petroleum jelly, which is a soft paste and contains a substantial proportion of oil. The former is largely used for coating metal and other surfaces for protection against the weather, storage, etc., and the latter also has applications of this sort. It is most familiar in its highly refined state as a base for a number of pharmaceutical and toilet preparations.

**The Petroleum Ceresin Group.**—The structure of this group is "micro-crystalline," and was formerly considered "amorphous." Ceresins are obtained from the naturally occurring "Ozokerite," and from certain petroleum residues. When a small amount of ceresin is mixed with paraffin wax, the resulting crystalline structure is much less well defined, and waxes used for electrical insulating and dielectric purposes frequently incorporate petroleum ceresin.

**Asphaltic Bitumen.**—Asphaltic bitumen is the name given to the residue from the distillation of certain crude oils. It may be regarded as a colloidal system in which colloidal particles of asphaltenes are dispersed in an oily medium, the disperse phase being stabilised by the resinous material present. If bitumen is heated and blown with air, we have "blown bitumen" produced. This is harder than the original product, and it has been suggested that additional asphaltenes are formed on blowing. The asphaltenes are generally supposed to be polycyclic compounds containing more or less aromatic nuclei, with sulphur or oxygen combined in some way. The asphaltic resins impart the important property of ductility to the mixture.

The tests by which bitumens are assessed are variations of viscosity tests. In the first, the "Ring and Ball" apparatus, the "softening point" temperature is determined at which a specified steel ball will fall through a ring mould of bitumen, drawing the bitumen down through a distance of one inch.

The second, the "Penetration Test," determines the distance in tenths of millimetres, to which a specific needle, when loaded to a total weight of 100 grams, will penetrate into the bitumen in 5 seconds at 25° C.

An empirical relationship between the two tests suggests that the softening point of any bitumen is the temperature at which it will have a penetration of about 800.

Bitumens are supplied "straight" or in the form of "cutbacks," *i.e.*, a mixture of bitumen with a suitable solvent such as a kerosene-creosote mixture. This enables the bitumen to be applied without having first to heat to a fairly high temperature. Bitumen is also available as an emulsion.

The chief uses are for road making, roofing felts, bitumenised paper, paints, pipe coating, and in electrical appliances.

### Manufacturing Processes

(1) **Distillation.**—The modern distillation plant, a typical flow diagram of which is shown in Fig. 6, operates continuously and produces simultaneously



from crude oil the following fractions:—(1) Light gasoline. (2) Heavy gasoline. (3) White spirit. (4) Kerosene. (5) Light gas oil. (6) Heavy gas oil. (7) Lubricating oil distillates. (8) Heavy residue, for fuel or asphalt.

The plant consists of two atmospheric pressure stages and one vacuum distillation stage, fractionation being achieved in multiplate distillation columns, with both "overhead" and "sidestream" products. The sidestream products are passed through "strippers" which themselves are plate columns, where the "light ends" are removed by steam stripping. The degree of fractionation is very good and the fractions are suitable for commercial products without redistillation.

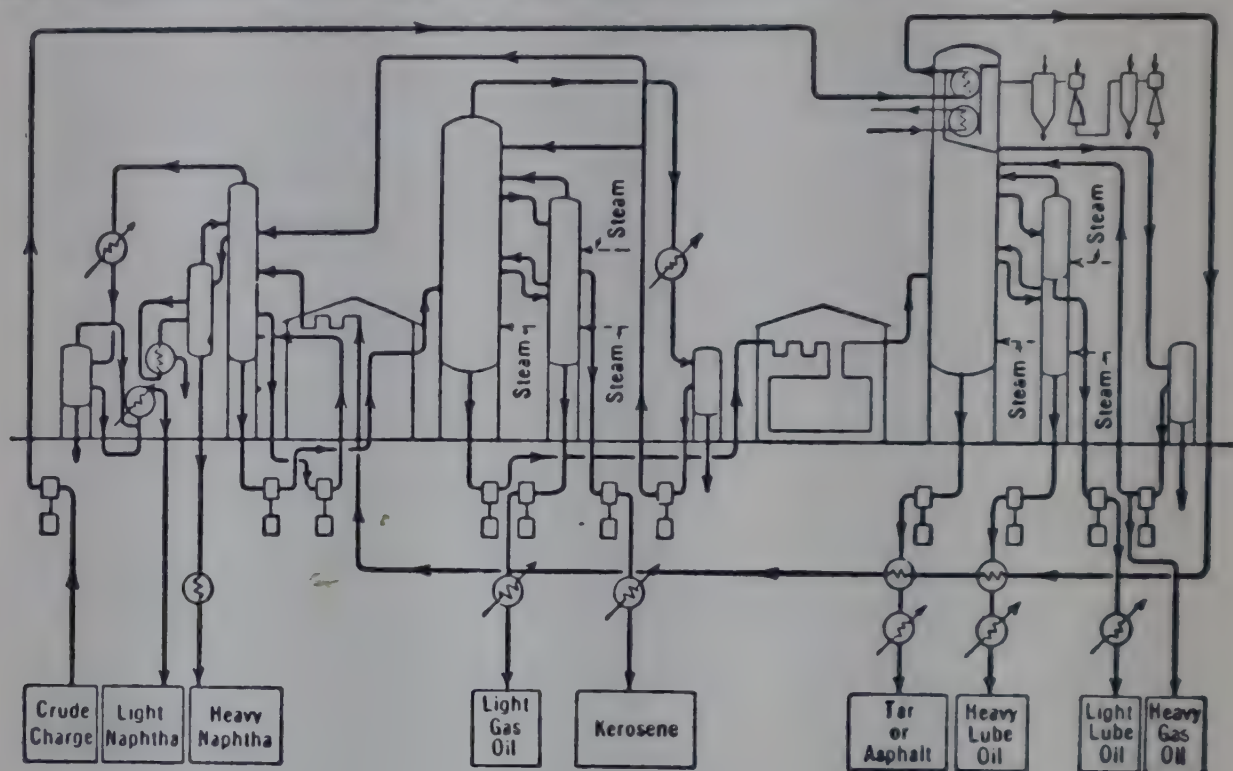


FIG. 6.—Three-Stage Distillation.

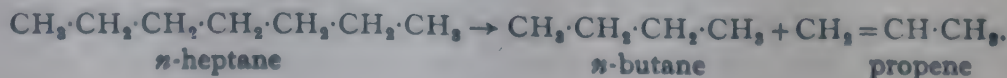
It is important that distillation temperatures do not exceed  $400^{\circ}\text{C}$ ., as thermal decomposition of hydrocarbons is appreciable above that temperature. In order to distil the lubricating oil fractions, column pressures of the order of 40 mm. mercury absolute are used in the vacuum distillation stage.

The continuous process makes possible efficient systems of heat exchangers and heaters, where each hot product leaving the plant contributes its quota of heat to the cold crude oil entering. The pipe-still furnaces are usually gas- or oil-fired, and the universal application of instruments and automatic controls makes for extremely steady conditions, with great economy of man-power. For instance, a plant distilling 5,000 tons per day may require no more than four men to conduct operations.

**Motor and Aviation Gasoline.**—Gasoline constitutes about 40 per cent. of the total consumption of petroleum products. As the gasoline fraction in crude oil amounts to between 3 per cent. and 25 per cent., according to the crude, more than half the total requirement is made by the process of "cracking." The general term "cracking" serves to describe the complex processes of decomposition, dehydrogenation, cyclisation, polymerisation, aromatisation, and so on, which occur when hydrocarbons are heated in excess of  $400^{\circ}\text{C}$ . with or without catalysts.

Typical reactions which take place during "cracking" are:

*Decomposition:*



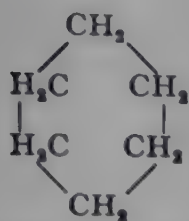


*Dehydrogenation:*

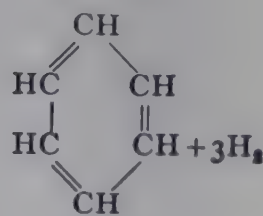
butene-1



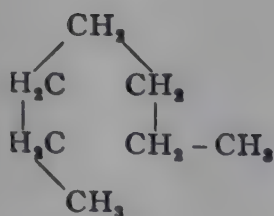
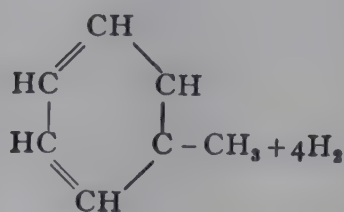
butadiene



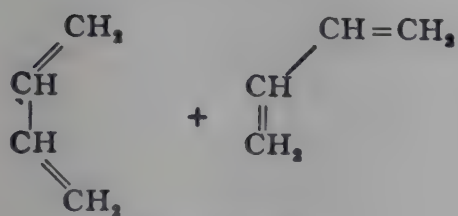
cyclohexane



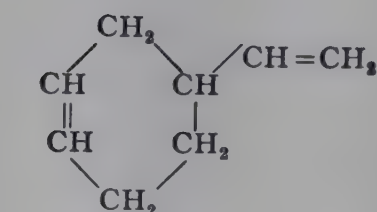
benzene

*Cyclisation:**n*-heptane.

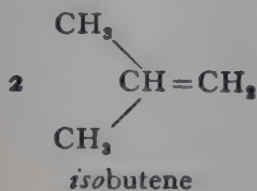
Toluene



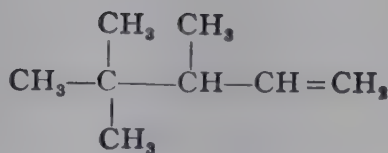
2 mols butadiene



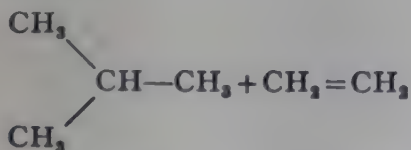
Vinylcyclo hexene

*Polymerisation:*

isobutene

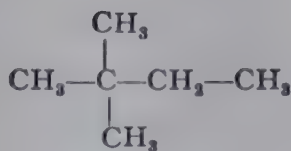


isooctene

*Alkylation:*

isobutane

ethylene



neo-hexane.

The thermodynamics and reaction kinetics of "cracking" reactions have been extensively studied, with the result that special processes have been devised for which the conditions of treatment are such that a particular type of reaction proceeds to an extent greatly in excess of undesirable side reactions.

Apart from the special processes which are described later, there are two main groups of "cracking" processes, "thermal" and "catalytic."

**Thermal Processes.**—Figs. 7 and 8 give the line diagrams for two plants, the first for the cracking of any base stock including residues from crude oil distillation, and the second for the "reforming" of a naphtha fraction.

In the first, the topped crude charge is preheated in the main fractionating column, and is pumped with the heavy fractions of the cracked product through

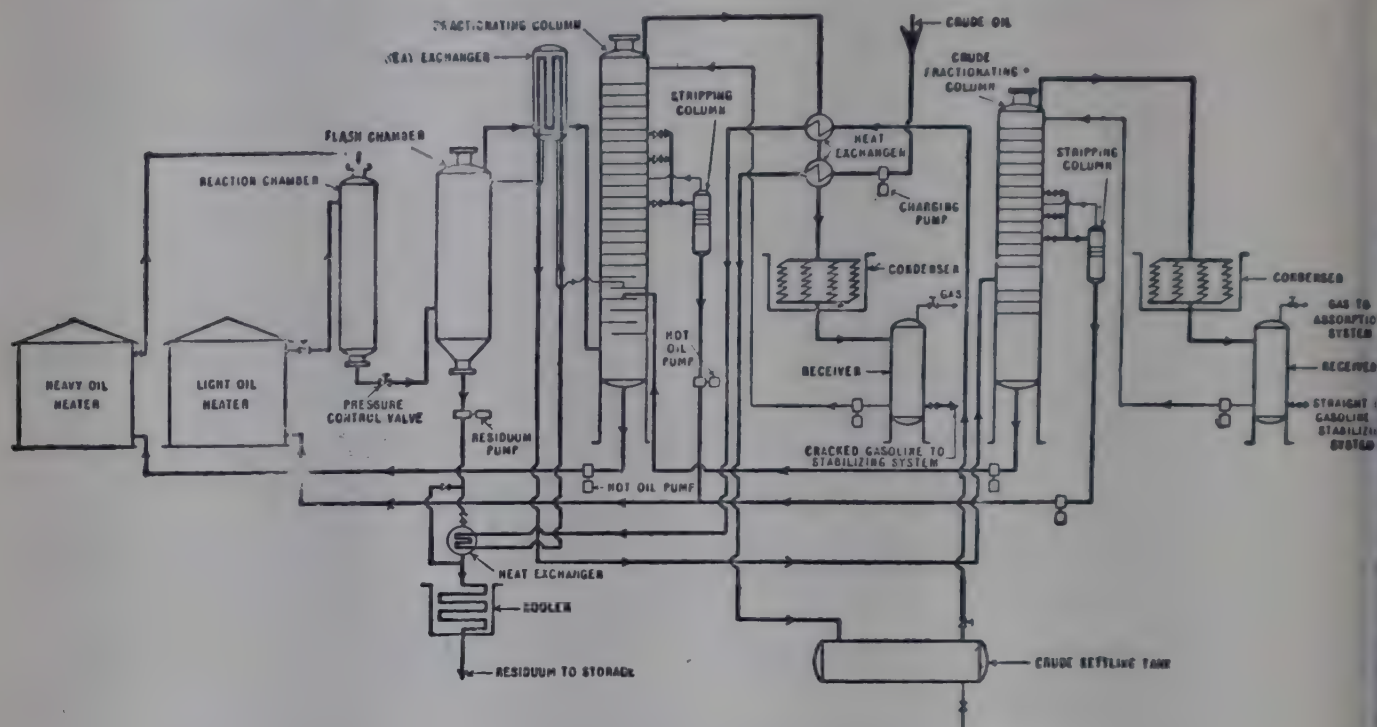


FIG. 7.—Flow Chart of Dubb's Selective Cracking System.

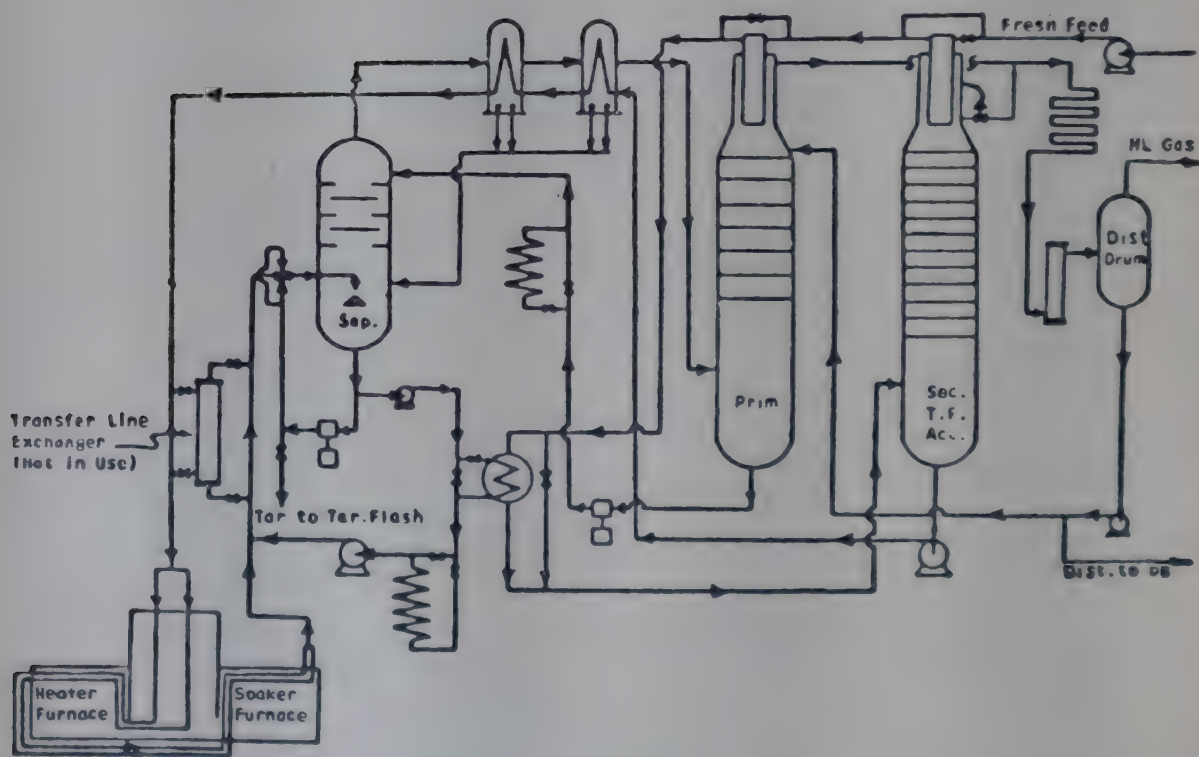


FIG. 8.—Reforming.

the first pipe-still furnace, at a temperature of  $520^{\circ}\text{C}$ . and a pressure of 600 lbs. per square inch. The overhead distillate from the flash chamber passes to the main fractionating column, where the gasoline fraction is removed as the overhead product. The recycle oil is drawn off as a sidestream product and is recycled through the second furnace—the products being fractionated as before.



This process is specifically designed for increasing the quantity of gasoline obtained from crude oil.

The reforming process, which has as charging stock a naphtha fraction of low octane number (40), produces a gasoline fraction of high octane number (80).

Reference to Fig. 8 shows that the reaction chamber of Fig. 7 has been replaced by the "soaking" section of the furnace. Cracking is an endothermic reaction, so that in the first section of the furnace the oil is raised to cracking temperature, and in the "soaking" section it is held at that temperature. The time factor is applied by the back pressure control valve, and the reaction is stopped by quenching. Cracking temperatures are about  $545^{\circ}\text{C}$ . with pressures of 750 lbs. per square inch.

**Catalytic Processes.**—The product from thermal cracking contains a large amount of unsaturates, both mono- and diolefines, and when sulphur is present in the charge stocks, the sulphur content of the product is high. Thermally cracked naphthas are usually considered unsuitable for aviation fuel base stocks. The olefine and sulphur content may be reduced by extensive treating methods, but this results in too great a reduction of anti-knock value.

Catalytic cracking produces a gasoline having, in general, a higher octane value and a lower sulphur content than thermally cracked stocks. Depending on the operating conditions, the product may contain a much lower percentage of olefines, the octane number of the product being partly due to the isomers and aromatics contained, so that treatment for the removal of objectionable olefines does not result in a too severe reduction of octane rating.

**Catalytic Cracking.**—The first successful catalytic process to deal with all the hydrocarbons in a wide boiling range stock was the Houdry process. The

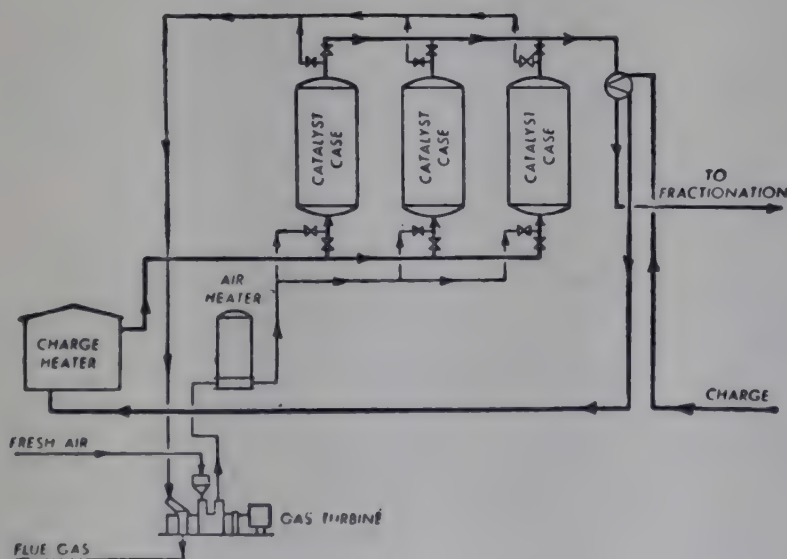


FIG. 9.—Houdry Catalytic Cracking Process.

flow sheet is simple (Fig. 9), but its success was only made possible by the high degree of mechanical ingenuity exercised in designing the control mechanism necessary for continuous operation. The feed stock is heated and admitted to a catalyst tower together with process steam at about  $450^{\circ}\text{C}$ . and a pressure of about 50 lbs., and passage through that tower is continued for about 10 minutes. The outlet vapours pass on for fractionation. At the end of 10 minutes, the first catalyst tower is shut off and a second one opened up to the process, while the

catalyst in the first is regenerated, the carbon being burnt off. The catalyst tower cycle is:

1. On stream—10 minutes.
2. Oil and vapour purge by venting to a condenser and steam jet evacuation system—5 minutes.
3. Regeneration with preheated air—10 minutes.
4. Air purge by steam jet ejectors—5 minutes.

All operations are automatic, even to the opening and closing of valves. During the process, the heat necessary to sustain the cracking reaction must be provided, and the heat evolved during the burning off of the carbon on the catalyst must be removed. These conditions are met by circulating a mixture of molten salts in finned tubes extending through the catalyst chambers, the catalyst being packed round the tubes. In this way the temperature of regeneration is limited to about  $530^{\circ}\text{C}$ ., and the temperature of cracking to about  $450^{\circ}\text{C}$ . The net result is an excess of heat which is utilised in a waste heat boiler to raise steam, and, finally, the hot gas from catalyst regeneration is used to drive the turbine which supplies the air to the catalyst chambers during regeneration.

In later plants, Houdry incorporated a second series of reactors, where the product from the first stage was again cracked. Octane numbers of nearly 100 were obtained at the second stage, against about 80 at the first.

The Houdry catalyst is a highly active aluminium hydrosilicate. The patents cover the use of hydrosilicates containing 70 to 80 per cent. silica, 20 to 10 per cent. alumina and not more than 10 per cent. of other oxides. Iron oxide  $\text{Fe}_2\text{O}_3$  is not to exceed 3 per cent. Nickel oxide may be present in amounts not exceeding 10 per cent., and a manganese compound (1 per cent.) may be added to facilitate regeneration. The catalyst is molded, dried and formed into pills or pellets  $\frac{1}{8}$ -inch diameter. The catalyst is said to operate for 180 stream days before replacement.

**The Thermoform Catalytic Cracking Process.**—The first Thermoform operated in 1942. In its essentials it is the same process as the Houdry process,

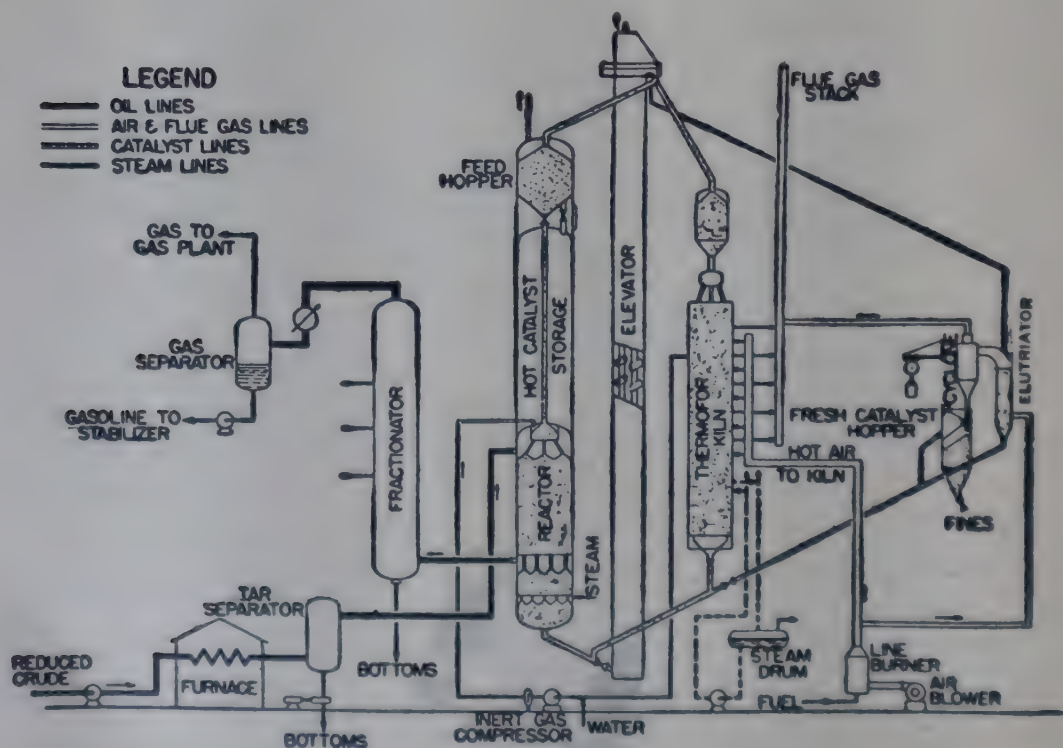


FIG. 10.—Simplified Flow Diagram of typical T.C.C. Installation Catalytic Section.



but reference to Fig. 10 will show that instead of having a number of "fixed bed" reactors the reactor is kept supplied constantly with a fresh supply of hot catalyst, the spent catalyst being continuously withdrawn and regenerated.

The fresh feed is heated in the furnace to about  $400^{\circ}\text{C}$ . to  $510^{\circ}\text{C}$ ., at a pressure of 10–15 lbs. per square inch. In the reactor, the vapours are intimately contacted with the catalyst, which flows down from the top over a series of baffles. After the reactor, the vapours pass on for fractionation. The spent catalyst is purged of oil vapours by superheated steam, and transported in a bucket elevator to the top of the regenerating kiln. In the regenerator, as in the reactor, the catalyst flows downward, passing through a series of alternate burning and cooling zones. Fresh air is admitted into each burning zone, regenerating the spent catalyst by burning off the carbonaceous deposit on it. The cooling zones between each burning zone are filled with steam generating coils to remove excess heat and to keep the catalyst temperature down below a maximum of  $620^{\circ}\text{C}$ .

The regenerated catalyst leaving the bottom of the kiln passes on to a second bucket elevator, which carries it up to the catalyst hopper above the reactor, thus completing the circuit.

**The Fluid Catalyst Process.**—If the two previously described processes appear to be remarkable feats of chemical engineering, the fluid catalyst process

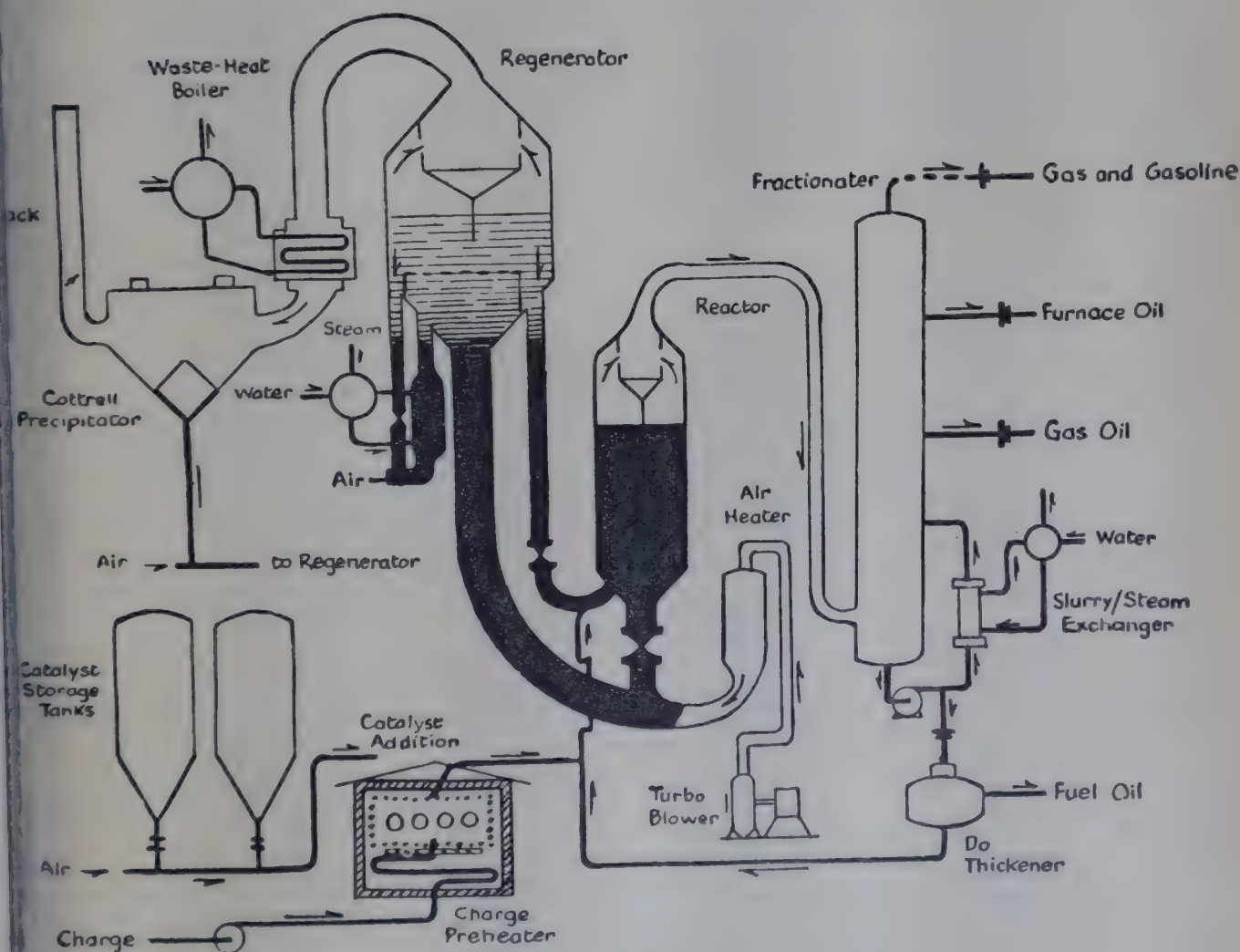


FIG. 11.

is in the superlative class. This process, the simplified flow of which is shown in Fig. 11, represents an entirely new engineering technique for contacting catalyst with oil vapours and for regenerating spent catalyst in a continuous operation. The catalyst is in the form of very fine grains, and by aeration by gas or vapour



behaves like a fluid. It will bubble up and support light objects on its surface and can easily be conveyed or will flow through pipe lines.

Dr Geoffrey Martin appears to have been one of the first to suggest this "fluidising" technique. In the last chapter of his *Treatise on Chemical Engineering*, published in 1928 (Technical Press, London), he described briefly but accurately the behaviour of fluidised solids and gives certain design data.

In the operation of the process, the preheated oil vapour produced by flash vaporisation enters a reactor, carrying along with it the catalytic material as a suspended powder. Because of the decreased velocity of vapours passing through the reactor, the suspended powder settles out to form a relatively dense, bubbling, bed. Cracking proceeds in this bed at a temperature of about  $480^{\circ}\text{C}$ ., as the rising oil vapours contact the active solid, and is completed in about 20 seconds. Product vapours then leave the bed, pass through a settling zone to a cyclone separator, carrying with them catalyst still in the form of a suspended powder. Here a large part of this suspended powder is recovered and returned through a small standpipe to the catalyst bed.

The vapours, substantially catalyst free, pass on for fractionation. Any remaining catalyst is recovered in the recycle oil.

The catalyst, separated from the cracked oil vapours, is withdrawn from the bottom of the reactor and discharged into an air stream which carries it in suspended form to a regenerator vessel. Because of the decreased velocity of the carrying gas, another violently bubbling bed is formed in this vessel, and the carbon is burned off at a temperature of  $590^{\circ}\text{C}$ . The purified catalyst is separated from the spent air, first in a settling zone above the bed and then in a cyclone separator, after which it is returned through a standpipe and control valve into the stream of hot oil vapour.

The complete cycle takes place without the use of a single mechanical moving part.

These three processes were the major factors in wartime's most important task, the production of aviation gasoline.

**The Production of Aviation Gasoline.**—At the height of the military campaigns of the war, U.S. refineries were called upon to supply aviation gasoline at the enormous rate of 16,500,000 gallons per day. It would have been impossible to provide this volume except for the use of tetraethyl lead and high octane blending agents which, when blended up with base stocks, served to bring the finished gasoline up to the specified octane number requirement. This varied between 87 and 100, according to the type of aircraft.

The base stocks were largely provided by the segregation of special fractions distilled from crude oil, or extracted by suitable solvents from certain distillate fractions, and from the products of catalytic cracking operations.

It is usually impossible from a practical standpoint to make an aviation fuel by the simple expedient of adding a knock-suppressing agent, such as tetraethyl lead, to a single base stock.

The required octane rating may be achieved in several ways, and these are listed as follows:—

- (1) Increase the lead susceptibility (*i.e.*, the degree of "response" to the addition of a certain amount of tetraethyl lead, measured by the increase in octane rating) of the base stock by the addition of certain compounds or by the elimination of sulphur compounds.
- (2) Increase the octane number of the fuel by blending in a certain amount of a compound or mixture having a very high octane number.
- (3) Increase the octane number by blending in compounds with high "blending octane" values. This is not the same as the preceding point. Some compounds, which have an octane number of about 90 by themselves, behave as though that octane number were 120–130 when blended in quantities of 20–40 per cent. with the base stock.



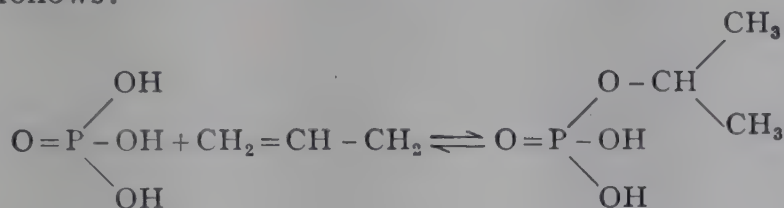
In practice, the methods used to bring the octane number of the base up to that required for the finished fuel are:

- (1) the addition of high octane compounds such as *isooctane* and *isooctane* mixtures, *isohexanes*, *isohexanes*, and *isopentane*, and
- (2) the addition of compounds whose blending octane numbers are sufficiently high to enable a relatively large increase in octane number of the blend when small percentages are added. Such compounds consist mainly of substituted benzenes and certain of the saturated cyclic compounds such as *cyclopentane* and *cyclohexane*.

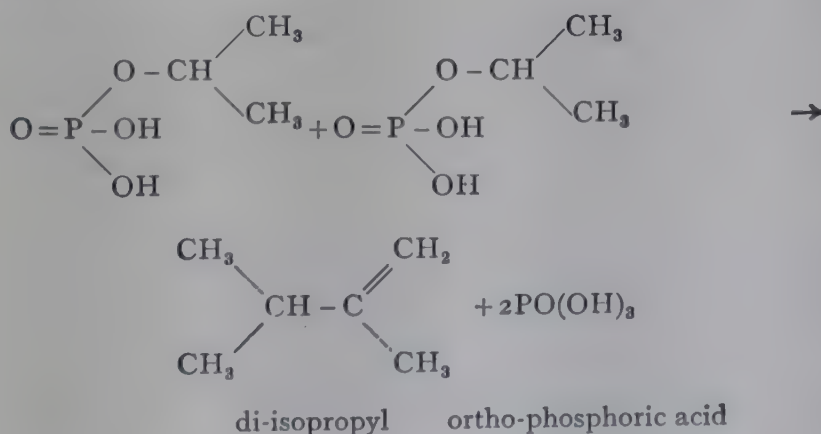
Some of the *isoparaffins* can be recovered from the crude oil. The rest must be manufactured. The process involved in manufacture may be summarised as follows:—

- (1) Polymerisation.
- (2) Alkylation.
- (3) Isomerisation.

**Polymerisation.**—This process was first devised for the catalytic polymerisation of gaseous olefines. The plant consisted of a heater, a number of catalyst towers, and fractionation equipment, and the catalyst used was phosphoric acid. The feed, mixed with the requisite water to prevent catalyst dehydration, was heated to only 205° C., and passed through a series of four catalyst towers. Owing to the exothermic nature of the polymerisation reaction, there was a temperature rise of about 70° C. The catalyst towers could be by-passed in turn for catalyst reactivation. The polymer gasoline had an octane number of about 80. With phosphoric acid catalyst, Ipatieff suggests the scheme of conversion was as follows:—



which decomposes as follows:—



This was the start of the many superb processes where, as the film commentator said, "The gently persuasive methods of catalysis replace the brutal methods of high temperature and high pressure."

In general, only unsaturated compounds will combine under polymerisation conditions, and the product or polymer is generally olefinic in character. Treatment necessary to improve stability would result in an uneconomical loss in octane number. In "selective polymerisation," using as charge material the  $\text{C}_3/\text{C}_4$  fraction from cracked gas, the resulting polymer products must be hydrogenated to form the saturated compounds, which are then excellent blending agents.

**Alkylation.**—This reaction consists of the combination of an olefine with an *isoparaffin* to produce a branched paraffin of higher molecular weight. The first process, the sulphuric acid process, is shown in Fig. 12. The *isoparaffin* and olefine mixture at 5° C. is fed to the reaction vessel, together with 98 per cent. strength sulphuric acid. The ratio of *isoparaffin* to olefine is kept high so as to prevent polymerisation of the olefine or other undesirable side-reactions. In practice this is attained by mixing recycled *isobutane* with the hydrocarbon feed before admixture with the catalyst.

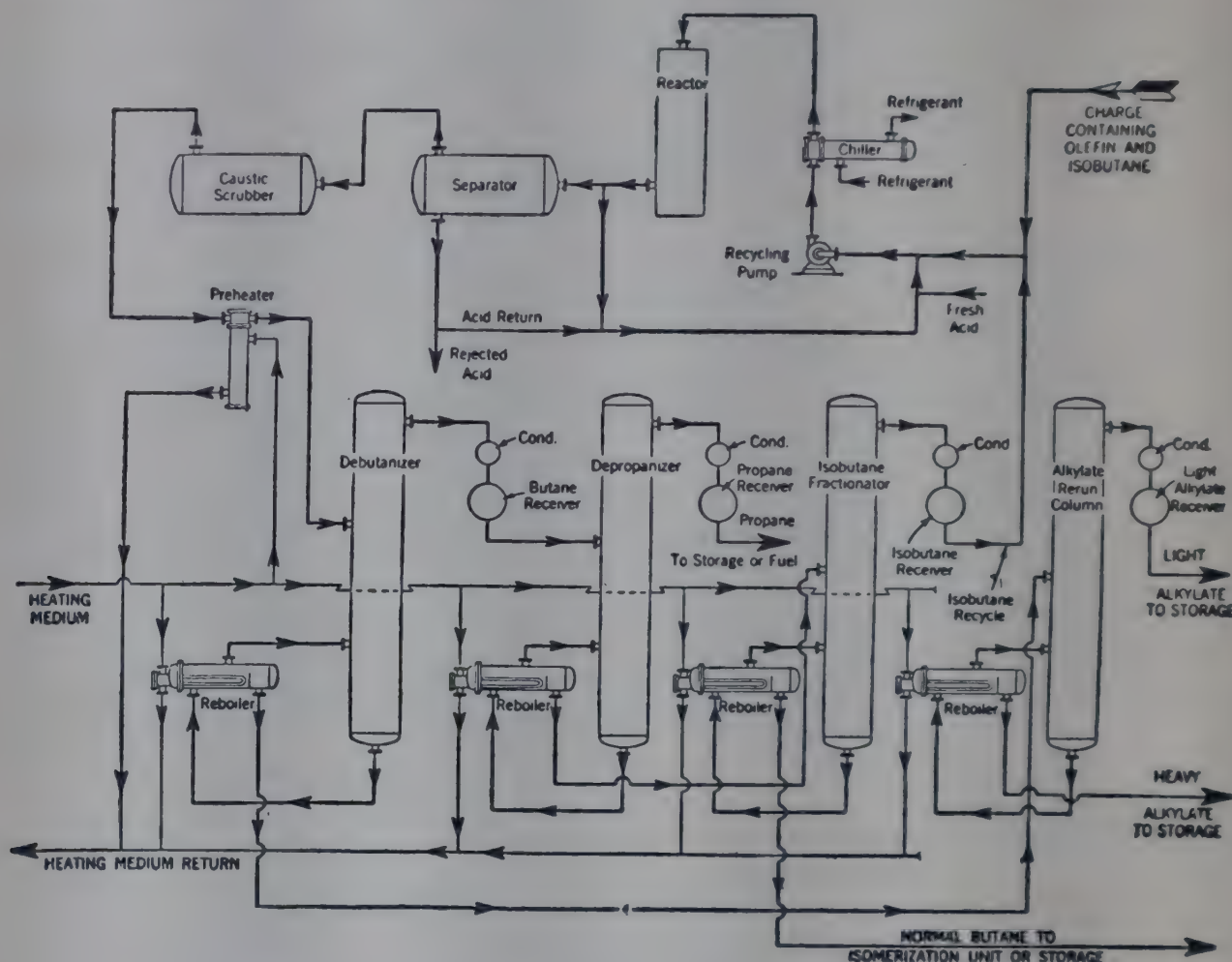
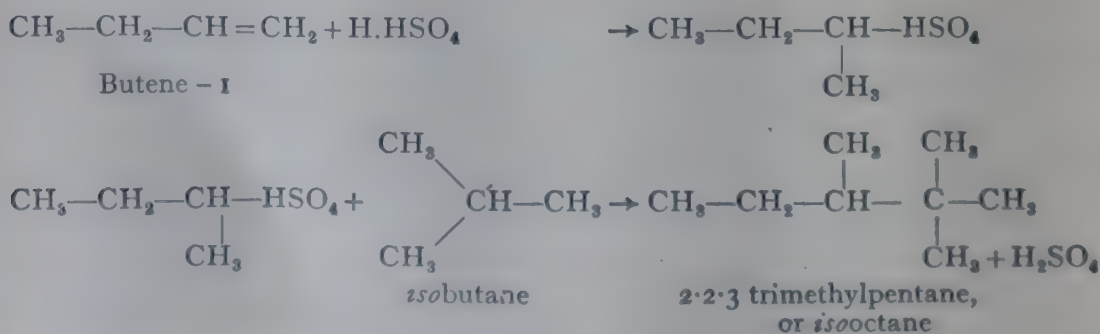


FIG. 12.—Flow Chart of Alkylation Process using Sulphuric Acid as Catalyst.

Following the reaction, the hydrocarbon mixture is caustic-washed and fractionated, first to remove *isobutane* which is recycled, then to recover *n*-butane for refinery fuel or for feed to the isomerisation plant.

Although there is not a definite agreement on the theory of the reactions in sulphuric acid alkylation, one explanation is that the reaction proceeds as follows:—



This is probably an oversimplification.

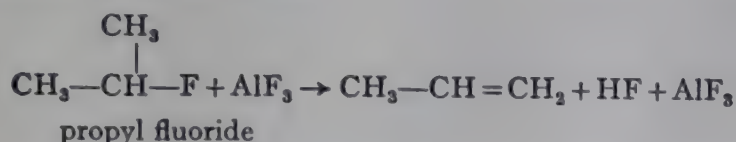


Disadvantages of the sulphuric acid process are (1) the refrigeration necessary to cool the feed before the reaction, and (2) the comparatively high sulphuric acid consumption, about 1 gallon of acid is needed for each 15 gallons of alkylate produced.

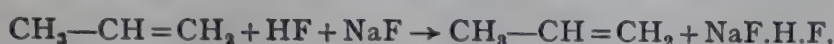
The finished "alkylate" usually consists of over 90 per cent. of the three trimethylpentanes and isopentanes.

Another version of the alkylation process uses hydrofluoric acid instead of sulphuric acid. The advantage of HF as an alkylation catalyst are said to be (1) the reaction can be carried out at normal atmospheric temperatures, eliminating the need for refrigeration, and (2) the ease of regeneration of the HF catalyst makes for high yields of alkylates in proportion to the amount of catalyst used.

The mechanism of the reaction is supposed to be similar to that with sulphuric acid. Any alkyl fluorides which have not reacted with isobutane are broken up by passing them over granular aluminium fluoride, decomposing into the corresponding olefines and HF, thus



The mixture of olefine and free acid is passed over solid, granular sodium fluoride, which forms an addition compound with the acid



The hydrofluoric acid is recovered from the addition compound by heating



It is desirable to use anhydrous HF to obtain the best results.

**Isomerisation.**—This process has been mainly used for the conversion of *n*-butane or *n*-pentane to the *is*o compounds, to provide feed stock for alkylation. It has, however, also been employed with a charging stock of a mid-continent *n*-hexane fraction, and gave, on recycle operation, a yield of about 90 per cent. of a product of 90 octane number. In the process shown in Fig. 13 the naphtha feed is carefully dried, and fed to the top of a hydrogen chloride absorption tower, then passes through a preheater to the reactor, together with hydrogen. The reactor is filled with aluminium chloride hydrocarbon complex catalyst. The effluent from the reactor, consisting of isomerised naphtha, hydrogen, hydrogen chloride and small amounts of catalyst, passes successively through a hot settler, a cooler, and a cold settler.

The catalyst is separated in the two settlers and returned to the reactor. Hydrogen and HCl are flashed off in the cold settler, and the rest of the HCl is removed in the HCl stripper. The liquid product from the HCl stripper is caustic and water washed and fractionated.

In butane isomerisation, the process is to pass the butane in vapour form, mixed with HCl, through a granular bed of  $\text{AlCl}_3$  catalyst. Subsequent separation is effected by compression, refrigeration and fractionation.

**Dehydrogenation.**—Dehydrogenation was developed for the purpose of converting butane to butenes for alkylation or polymerisation, but also for the conversion of butanes or butenes to butadiene for synthetic rubber manufacture.

Dehydrogenation is accomplished by passing the preheated hydrocarbon vapours under controlled conditions of space velocity, temperature and pressure over catalysts such as chromic oxide supported on alumina, in pellet form. Reaction temperatures are about  $550^\circ$ – $650^\circ$  C., with about 20 lbs. pressure. The form of plant is similar to that of the Houdry catalytic cracking process (*q.v.*). The products of dehydrogenation containing butenes, unconverted butane and a small proportion of lighter hydrocarbons, are cooled, compressed and the  $\text{C}_4$

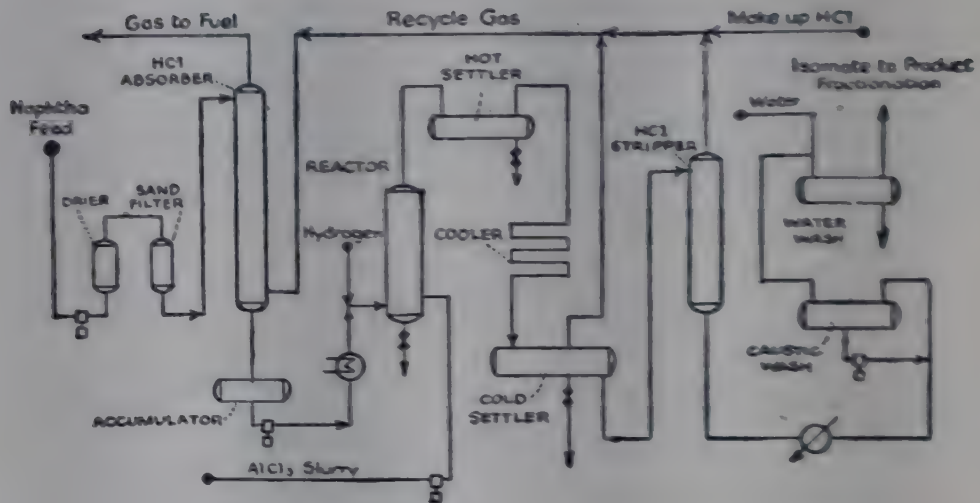
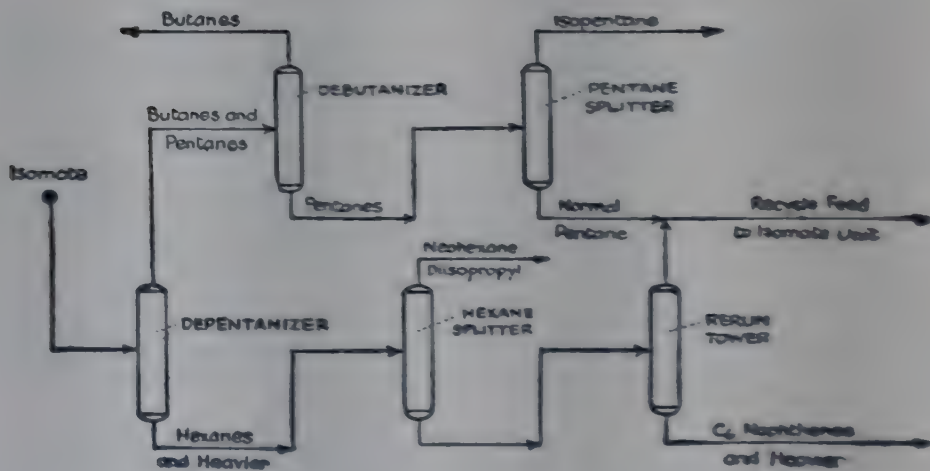
INDIANA ISOMATE REACTION PROCESSINDIANA ISOMATE FRACTIONATION PROCESS

FIG. 13.



fraction separated and fractionated. The unconverted butanes are recycled back to the process.

By blending together the various products, the production of which is described above, in the approximate proportions:

Base stock . . .	70 per cent.
Blending agent . .	30 „
Tetraethyl lead, 4 cc. per gallon.	

the enormous demand for aviation fuel was met.

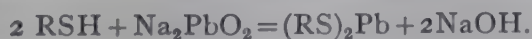
**Chemical Refining of Gasoline.**—Gasoline fractions, whether “straight run” or “cracked,” usually contain sulphur compounds, often in the form of mercaptans. There may also be present highly unsaturated compounds such as di-olefines which readily form gumming products on storage. These must be eliminated.

The main processes in use for the removal of the mercaptans, or for “sweetening” the distillate, are:

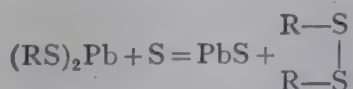
- (1) Sulphuric acid treatment.
- (2) Sodium plumbite and “Doctor” treatment.
- (3) Sodium hypochlorite.
- (4) Solvent extraction methods.
- (5) Catalytic removal processes.

Sulphuric acid has been used in the refining industry for nearly 100 years. It reacts with certain constituents of the oil fractions, forming a heavy “acid tar” or “acid sludge,” which settles and may be removed. The way in which sulphuric acid operates may be either by oxidation, as in the transformation of mercaptans to disulphides; by polymerisation, as with di-olefines, or as a solvent, as with sulfoxides and sulphones. The gasoline, after acid treatment, is washed with water and then redistilled, so as to eliminate the high boiling polymers. “Straight run” spirit may be treated with a small amount of 94 per cent. strength acid, but “cracked” spirits, because of the large amount of olefines present, are treated with about 80–85 per cent. strength acid at a low temperature and for a short time, so as to minimise loss.

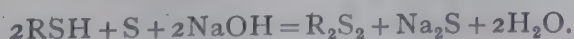
The “Doctor” process, for “sweetening” gasoline, is a method whereby the foul-smelling mercaptans are converted to relatively innocuous disulphides,



Some of the lead mercaptides remain in solution in the oil, and to eliminate these, a little sulphur is added.



The alkyl disulphides are still soluble in the oil, but are no longer foul-smelling, hence the name of the process, “sweetening.” The sodium plumbite is regenerated by heating the lead sulphide with water and blowing with air, to form lead sulphate, then sufficient caustic soda is added to give the sodium plumbite once again. The whole “sweetening” reaction may be given as



The use of sodium hypochlorite solutions for refining of gasolines dates from about 1918. The reaction is one of oxidation, mercaptans forming disulphides, sulphides forming sulphones, etc. The process is carried out in counter current “washers,” i.e., alternate mixing and settling. The hypochlorite working solution is adjusted to about 0.3N, with an alkali content of about 1.0 gm. per litre. After treatment the gasoline is washed with water, and is then suitable for use.



With all the above processes it is usual to give a preliminary treatment with caustic soda to remove hydrogen sulphide. If this is not done, elemental sulphur is formed in the subsequent refining operations, and this is most troublesome to remove.

In recent years, several solvent extraction processes have been put into operation. One such process, the "Solutiser" process, is shown in diagrammatic form in Fig. 14. The mercaptans are extracted, using as extraction solvent a solution of potassium *isobutyrate* in caustic soda. The extraction, which takes place in a packed column, is counter current, the solutiser solution being subsequently regenerated and freed from mercaptans, which are recovered. A similar process, the "Unisol" process, uses a solution of methanol and caustic soda as solvent.

The Houdry catalytic cracking process (*q.v.*) may be adapted for catalytic desulphurisation. The distillate to be treated is vaporised and passed to the catalyst chambers at temperatures of 310° to 340° C., the sulphur compounds are adsorbed on the catalyst and removed as H<sub>2</sub>S or SO<sub>2</sub> during the regeneration process. The catalyst consists of a preparation of hydrated aluminium silicate, with certain metallic oxides such as nickel and cobalt.

Bauxite is used as a catalyst in the process shown in Fig. 15. The feed stock is vaporised and passed to the catalyst tower at 380° C. Mercaptans, sulphides and disulphides are removed in the process, cyclic compounds are not greatly affected.

**The Analysis of Cracked Gasoline.**—For the evaluation of cracked gasoline, it is necessary to estimate the quantities present of unsaturated hydrocarbons, aromatics, paraffins and naphthenes.

The best method for determination of olefine content is by the so-called "bromine number." This is a measure of the amount of bromine in grams which will combine with 100 grams of the oil the conditions being such as to keep the degree of substitution reactions at a minimum. In the procedure laid down by the Institute of Petroleum (Method I.P. 9/42), the sample is reacted with a solution of bromine in carbon tetrachloride, the amount reacted being calculated by titrating the excess with thiosulphate after the addition of potassium iodide. After the first titration, potassium iodate is added to the solution, which is again titrated with thiosulphate. This latter titration gives a measure of the amount of bromine combined in substitution reactions, which must be allowed for.

The percentage of unsaturated hydrocarbons is calculated according to the following formula,

$$U = \frac{M.N.}{160}$$

When N = bromine number

M = mean molecular weight.

The aromatic content may be found according to the Institute of Petroleum (Method No. I.P. 3/42). The method depends on the aniline point/aromatic content relationship, allowance being made for the degree of unsaturation as determined by the bromine number.

The aniline point of the sample is found, before and after sulphonation with 99 per cent. H<sub>2</sub>SO<sub>4</sub>. To the rise in aniline point is applied a correction factor based on the bromine number, and the aromatic content is read off from tables supplied.

The so-called PONA analysis of Universal Oil Products (U.O.P. Method H—173-40) is an excellent way of determining the quantities of Paraffins, Olefines, Naphthenes, and Aromatics (hence PONA).

The procedure consists essentially of determining the percentage of olefines



from the bromine number and molecular weight, and the aromatic hydrocarbons by specific dispersion, calculating the naphthene-paraffin ratio from the refractive index of the total sample and the percentage of aromatic hydrocarbons and

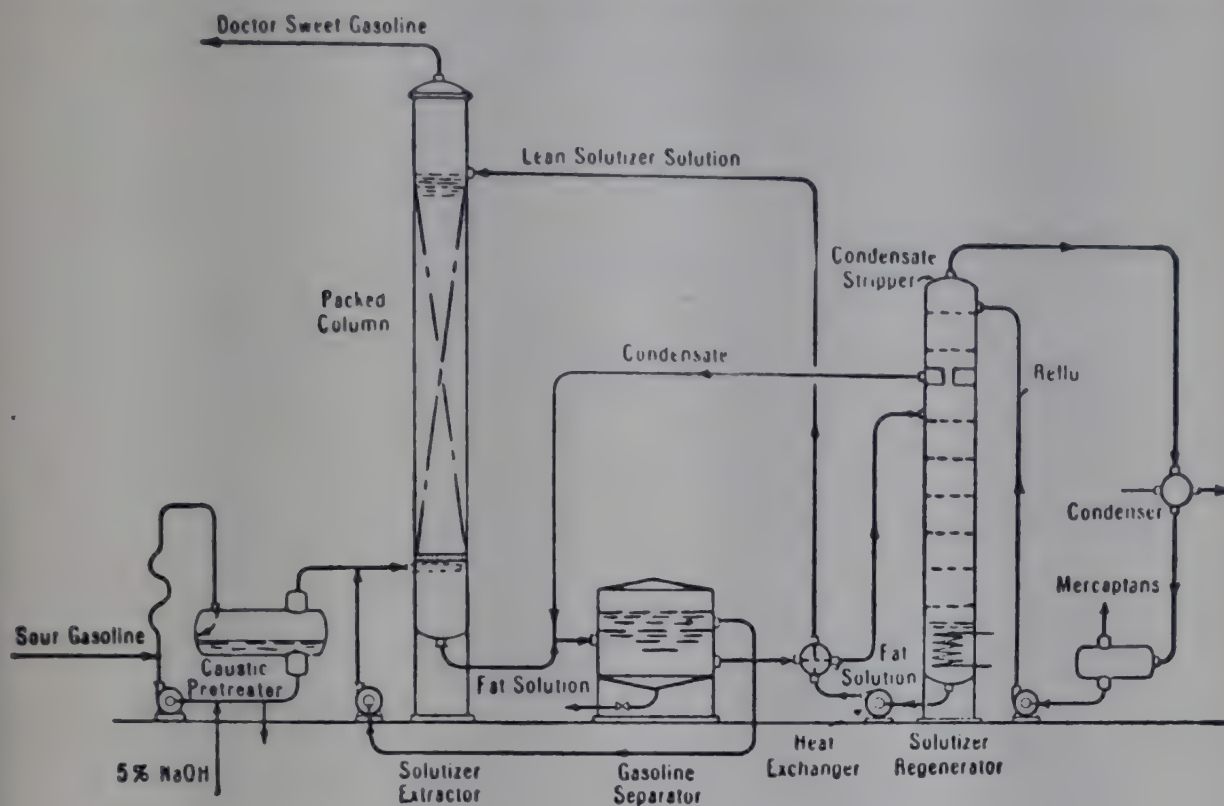


FIG. 14.—The Solutizer Process.

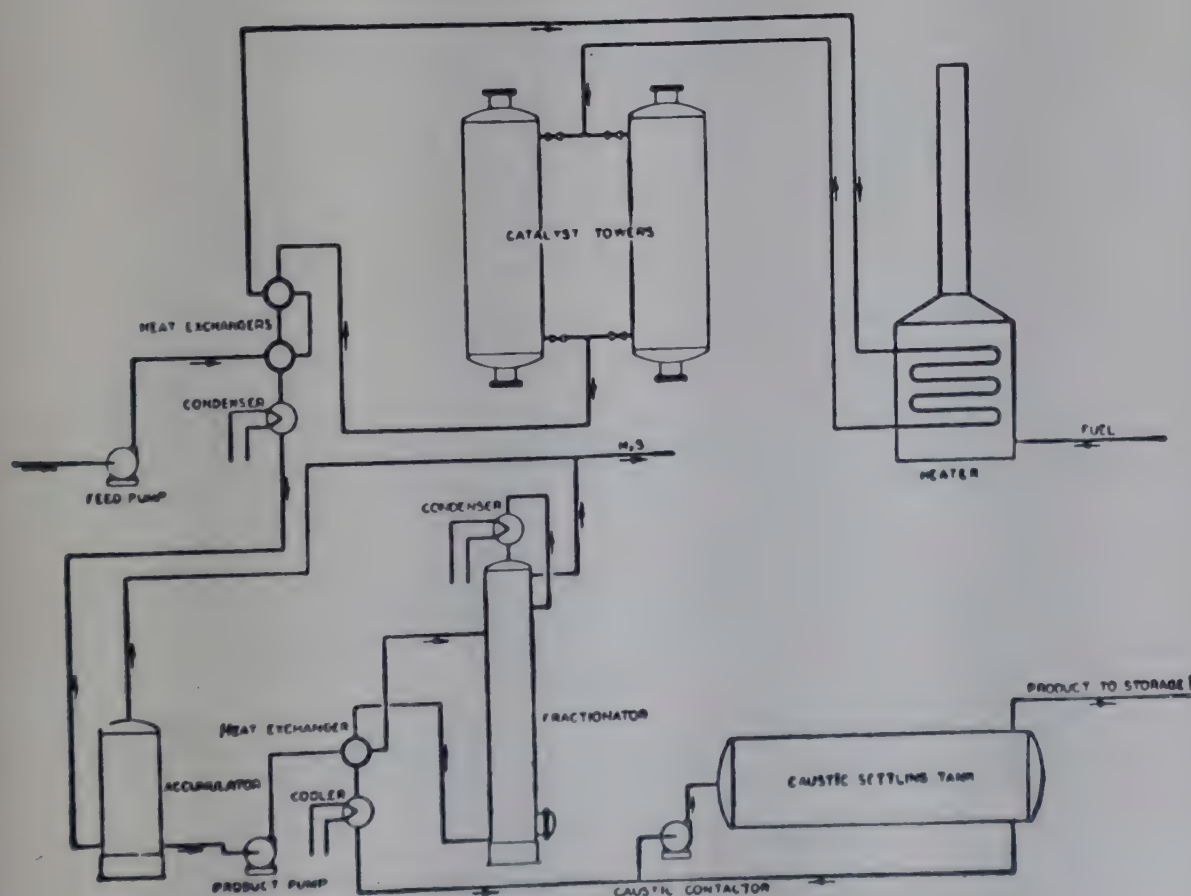


FIG. 15.—Catalytic Desulphurisation Process.

olefines. Charts and nomographs have been prepared which makes this determination quite rapid.

For the identification and estimation of individual hydrocarbons, it is now usual to employ spectroscopic methods. All hydrocarbons absorb in the infra-red and

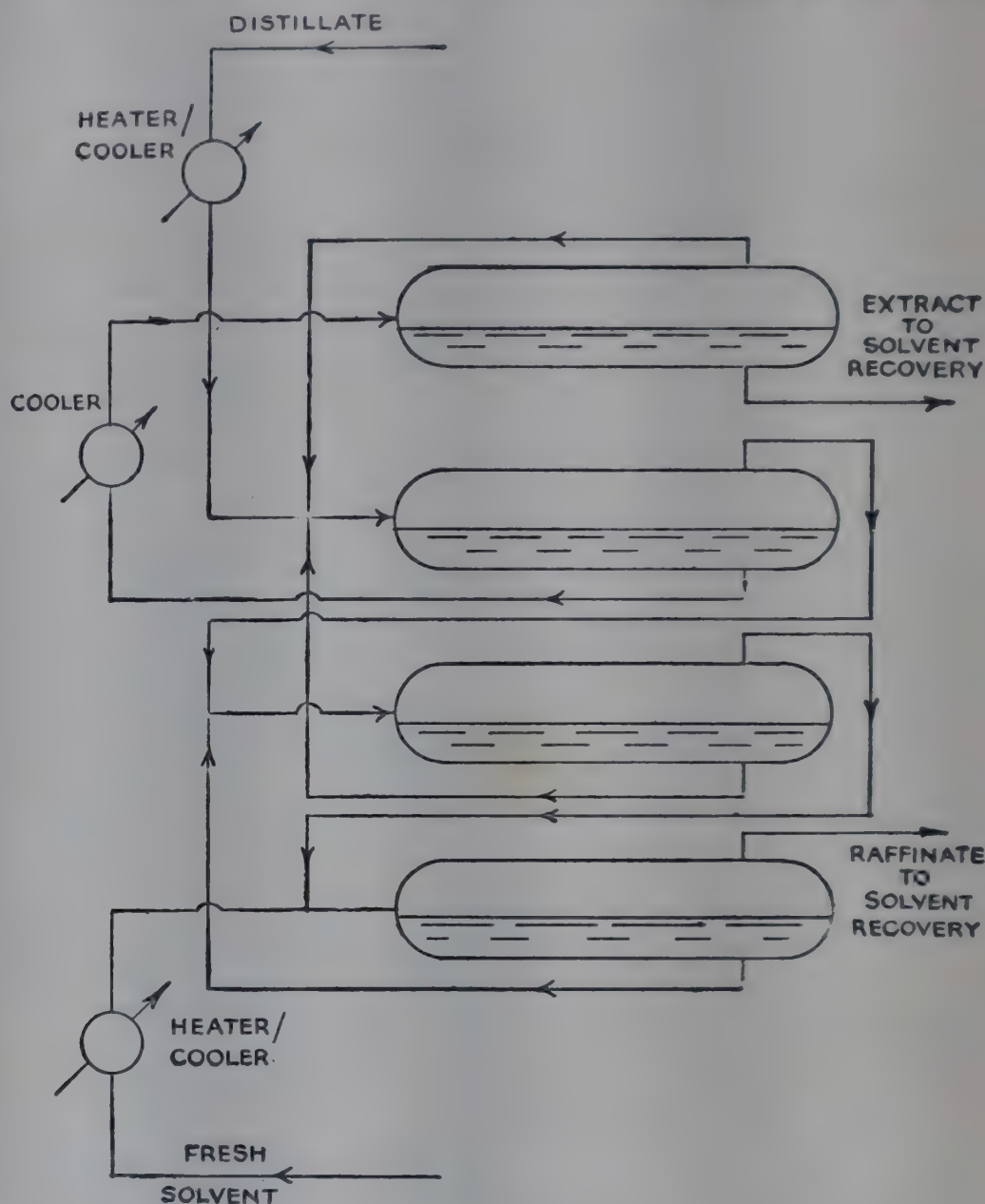


FIG. 16.

far ultra-violet, but while aromatic hydrocarbons absorb in the near ultra-violet (2500–3000 Å), saturated paraffins and naphthenes do not. A sufficient literature now exists as to the absorption spectra of many of the aromatic compounds to make identification a simple matter.

The range of infra-red analyses which is considered practicable at present in the industry includes the paraffin gases from  $C_1$ – $C_5$ , and the olefines up to  $C_4$ . The liquid paraffin mixtures up to the octanes have been analysed as well as the aromatics up to  $C_8$ .

As an example of the speed and accuracy of determination, a 5-component mixture containing benzene, *n*-hexane, 3-methylpentane, methylcyclopentane and 2,2 dimethylpentane can be analysed in 90 minutes.

**Kerosene.**—Kerosenes may be divided into two groups, burning oils and power kerosenes.

Reference has already been made to the desirable properties of a burning oil. Suitable distillates of the paraffin base type need little refining, a treatment with



a small amount of sulphuric acid, followed by washing and percolation through fuller's earth or bauxite is sufficient to produce a good burning oil.

For intermediate and naphthene base stocks, the problem of refining is more difficult. The presence of compounds with a high carbon-hydrogen ratio causes the oil to burn with a smoky flame, and removal or reduction of these compounds by treatment with acid necessitates the use of large quantities of acid and entails high losses.

A commercial method of solvent extraction for the removal of aromatic compounds was first introduced by L. Edeleanu in 1909, the process being applied to the refining of Roumanian kerosene. In the extraction process, the elements of which are shown in Fig. 16, the distillate is extracted counter-currently with liquid sulphur dioxide, which is an excellent solvent for the more aromatic constituents of the oil. The resulting mixture forms a two-phase system, the  $\text{SO}_2$ -aromatic mixture forming the lower layer in the settlers. The upper layer, known as the raffinate layer, after removal of the solvent, has excellent qualities as a burning oil. A simple treatment with fuller's earth or bauxite is given as a finishing process.

The more aromatic constituents, known as "extract" after removal of the  $\text{SO}_2$ , are usually blended with gasoline or power kerosene, in which the presence of aromatic compounds is desirable.

For power kerosene, distillates from naphthene base crudes are more desirable, because of the higher octane rating. Little refining is necessary in most stocks from which power kerosene is made, a small sweetening treatment usually being considered sufficient.

**Compression Ignition Engine Fuels.**—In the high speed C.I. engine, the best fuels, *i.e.*, those with the least "ignition delay," are obtained from paraffin stocks. The low speed stationary engines are much less selective with respect to the fuels consumed.

The specification for a high speed engine fuel calls for a distillate of which 90 per cent. must distil over below  $357^\circ \text{C}$ ., the sulphur content must not exceed 1 per cent., nor the viscosity 6 centistokes at  $100^\circ \text{F}$ .

Since the price of diesel fuel is relatively low, it is customary to manufacture these oils from a type of crude which gives a suitable product directly on distillation, or after the minimum of treatment. Since paraffin base distillates have a high diesel index, but tend to precipitate wax, and naphthene or intermediate base crudes have a lower diesel index but are wax free, a blend of both or all types is often supplied.

**Lubricating Oils.**—Lubricating oils may be divided into four classes:—

- (1) Industrial lubricants not subject to extreme conditions of heat and pressure.
- (2) Lubricants which must possess good stability at high temperatures, as in the internal combustion engine.
- (3) Dark viscous oils for slow-moving machinery, and for axle lubrication, etc.
- (4) Special oils, such as hydraulic oils, etc.

The degree of refining is appropriate to the service.

For the first group it is customary to start with a distillate of suitable viscosity characteristics, and refine it so as to achieve a sufficient stability to storage. The process may consist of a treatment with 1.5 per cent. sulphuric acid, followed by clay treatment.

The acid treatment may be carried out in large acid agitators, where the acid and oil are mixed by blowing with air, the sludge being settled out and withdrawn; or it may be a continuous process, the mixing of the oil and acid taking place in a pump or orifice mixer, and the separation of sludge and oil being brought about by passing the mixture through a centrifugal separator. The latter process is now in common use for the treatment of the more viscous oils.

The residual acidity of the oil may then be removed by neutralisation with lime or by adsorption on fuller's earth. As the final process in the treatment of lubricating oil is the "bleaching" with fuller's earth, the neutralisation process is carried out simultaneously with this clay treatment.

Percolation methods which are used for gasoline and kerosene are replaced by the "contacting" method. The fuller's earth is ground to a 200 mesh powder, mixed with oil in proportions 1-6 per cent., heated up in an agitator, and finally filtered. Greatly improved results have been obtained using the "High Temperature Clay Treatment" process, which is shown in Fig. 17. The effect of time and temperature on the bleaching properties of fuller's earth is shown in the table on page opposite.<sup>(14)</sup>

Reference is made above to "Activated Clays." These are clays which have been "activated," *i.e.*, had their bleaching efficiency greatly increased by treatment with acid, washing and drying. The best bleaching clays formerly came from Florida, but the "activation" process made possible the successful use of clays from Bavaria, and Redhill, Surrey, among other places, so that most countries now have an indigenous source of these bleaching earths.

When a distillate contains paraffin wax, this must, of course, be removed. Oils of relatively low viscosity from which, when chilled, the wax separates out in well-defined crystals, may be filtered directly, the wax forming a filter cake. Such a distillate is known as a "pressing cut." For oils of higher viscosity, and oils from which the wax does not separate in well-defined crystals, other methods of dewaxing are applied.

The first of these employs centrifuges to separate the wax from the chilled oil, previously diluted with a suitable solvent,

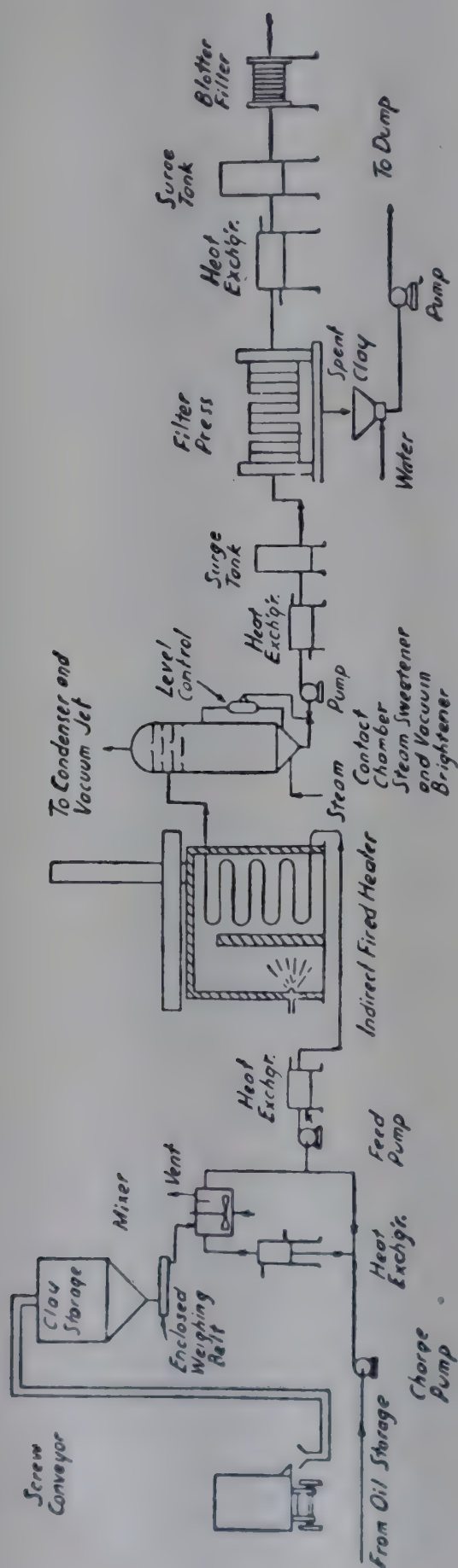


FIG. 17.—Flow Diagram for Continuous Contact Filtration Plant.



Treating Temperature. °C.	Time at Maximum Temperature. Minutes.	Colour Intensity.	
		3 per cent. Activated Clay.	8 per cent. Natural Clay.
260	0	322	255
	30	170	165
	60	150	165
	200	125	185
315	0	163	160
	30	91	125
	60	84	115
	200	76	108
370	0	108	146
	30	66	119
	90	68	119

such as a light naphtha. The oil-naphtha solution and the wax are discharged separately from the centrifuge, the wax being carried away with a "carrier liquid," usually hot water. The naphtha is then distilled from the oil, which

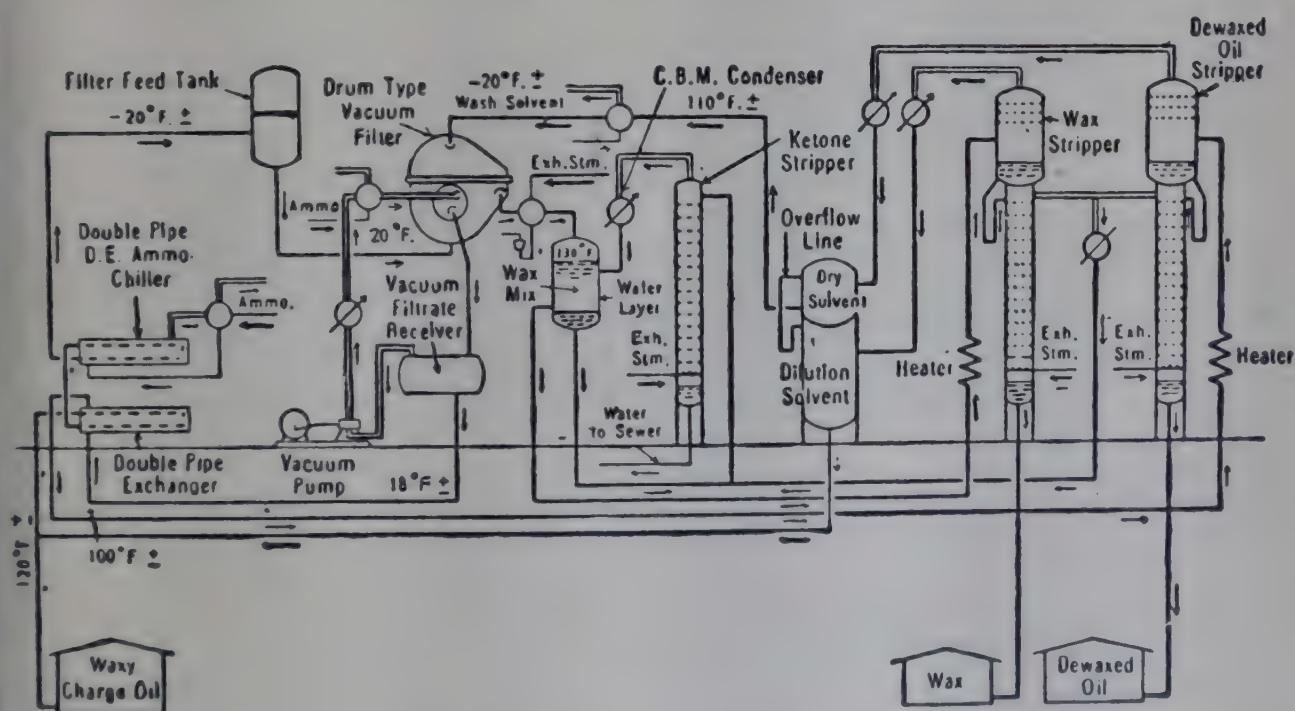


FIG. 18.—The Solvent Dewaxing Process.

goes forward for further treatment, the naphtha being recycled. The melted wax is separated from the water, and may then be diluted with more solvent, and again put through the process, this second stage being designed to reduce the oil content of the wax. There are two disadvantages to this process; first, it is necessary to chill to 20°–25° C. below the desired pour point of the oil, and second, it does not work very well with the more crystalline waxes.

Centrifuge dewaxing has now largely been replaced by the so-called "solvent

dewaxing" process. In this process, the waxy distillates are dissolved in a solvent or mixture of solvents, chilled to the desired temperature at which the wax is insoluble, so that it may be filtered off, usually on rotary filters. Fig. 18 shows the flow sheet of one such dewaxing process, which uses a mixture of benzol and methylethyl ketone as dewaxing solvent. A similar process employs a mixture of benzol and  $\text{SO}_2$ . These processes have the advantage that it is not required to chill more than about  $5^\circ \text{C}$ . below the desired pour point of the oil. A third process employs propane as solvent, and although it is necessary to use lower temperatures, it is possible to achieve these by direct evaporation of the solvent, so that external chilling is avoided.

The solvent dewaxing process is often used in conjunction with solvent extraction plants, which are employed in the manufacture of lubricants of the class (2) type, which must have good stability and viscosity/temperature characteristics.

Mention has already been made of the application of solvent extraction to the refining of kerosene. About 1927, it was applied to the treatment of turbine oils, and soon afterwards was used for the extraction of lubricating oil distillates in general. Distillates from certain crudes, such as Pennsylvanian oils, possess naturally the necessary qualities for premium lubricants, but following the introduction of the solvent extraction process, it was possible to make excellent oils from many other crude stocks.

Sulphur dioxide was the first solvent used, and there are now plants operating which employ the following solvents:—

- (1) Liquid  $\text{SO}_2$ , or  $\text{SO}_2$ /benzol.
- (2) Furfural.
- (3) Phenol, or phenol/water.
- (4) "Chlorex."
- (5) Liquid propane (for de-asphaltising).
- (6) Nitrobenzene.
- (7) "Duo-Sol."

All the processes were basically the same; the mixture of oil with solvent, the settling into two layers, separation of the layers and recovery of solvent. In the liquid propane process, the "raffinate," *i.e.*, lower carbon/hydrogen ratio hydrocarbons, mixes with the bulk of the solvent, the "extract" phase consisting mostly of the high specific gravity hydrocarbons associated with only a little solvent. In all the other processes, the bulk of the solvent is associated with the extract phase.

For highly viscous and high molecular weight oils, the Edeleanu process was modified and a mixed solvent,  $\text{SO}_2$ /benzol was used. The addition of benzol has the effect of enabling more to be extracted compared with pure  $\text{SO}_2$  at the same temperature, although as a consequence the selectivity suffers.

In the Duo-Sol process, two solvents are used, but they are not miscible. The solvents are "selecto" (cresylic acid) and liquid propane. In operation, the liquid propane and the "selecto" are fed to opposite ends of a counter current system, and the oil feed stock is injected at an intermediate point somewhat nearer the propane inlet than the "selecto" inlet end of the system.

The system thus comprises in effect a stripping section in which the outgoing raffinate is stripped by the "selecto" of the "aromatic" constituents remaining therein, and a rectifying section in which the extract is freed from paraffinic constituents by washing and refluxing back with propane. The Duo-Sol process is usually considered better with residual stocks.

**Transformer and Cable Oils.**—Transformer oils are almost invariably manufactured from naphthene base distillates, and there are two distinct methods of treatment.



The first and older method consists of a treatment with 5-10 per cent. of sulphuric acid, followed by the removal of all traces of reaction products. This is usually done by water washing and contacting with clay.

Transformer oil must have all polar compounds removed, to ensure the correct insulating properties, and must conform with specified stability test. It is therefore particularly important to eliminate the last traces of calcium sulphonate, which may have been formed during the refining process, since this compound acts as a strong pro-oxidant.

Oils for which is demanded a very slow sludging value, as called for in British Standards Specification A30, are refined with fuming sulphuric acid, the resulting oil soluble sulphonates being extracted with aqueous alcohol, before finishing off with clay in the usual way. The A30 grade is normally water white.

In some countries the amount of acidity developed in the oil after a period is considered more important than the initial sludge value, and it is found that oils which are highly acid treated, develop a greater degree of acidity.

Many transformer oils are now produced by the solvent extraction process, as previously described. Sulphur dioxide is considered particularly good for this purpose. This completely eliminates acid treating, and the acidity development on "ageing" is very low.

A good transformer oil in a well-designed transformer will last up to fifteen years.

Cable oils, which have very high viscosities, must also be free of polar compounds, and be resistant to oxidation. Most oils of this type are manufactured from naphthene base distillates, being given a heavy clay treatment either with or without prior solvent extraction, according to the stock.

**Petroleum Waxes and Ceresins.**—The process of dewaxing, already described, produces a "slack" wax, *i.e.*, a mixture of wax and oil containing up to 40 per cent. oil. This oil content may be reduced by "re-running" the wax with more solvent, and this "re-pulping" process, as it is called, is often incorporated in the dewaxing plant. In order to produce crystalline waxes free from oil, the process of "sweating" has been devised.

This consists, briefly, of chilling the slack wax to a solid mass and then gradually raising the temperature. It is suggested that, in the solid state, the wax crystals still have many voids in which the oil is contained. As the temperature is gradually raised, the cells are opened and the entrained oil drains away.

The plant used, known as "sweating ovens," or "sweating stoves," consists of shallow tanks, the bottoms of which taper down to an outlet pipe, and have above the taper section a strong wire mesh "floor." The tank is fitted with a large number of small bore pipes through which water may be circulated. A charge of melted slack wax is run into the tank, on to the surface of a layer of water which just covers the wire mesh. Cold water is then circulated through the coils, so that the slack wax becomes solid. The temperature of the circulating water is then gradually raised and, after first running off the water from inside the tank, the "sweated" oil, known as "foot's oil," is run off. As the temperature rises a second fraction is withdrawn, this usually being recycled in with the next charge of slack wax. The wax finally left is then melted and withdrawn, being known as "sweated scale." This is usually clay treated, and finally made into cakes in a slabbing press.

The process of "sweating" is usually confined to crystalline waxes, the micro-crystalline variety or petrolatums are de-oiled, using the centrifuge method. The resulting waxes may then be clay treated or, in the case of the more highly refined pharmaceutical products, acid and clay treated.

For the so-called petroleum ceresins it is important to have a very low oil content, the wax from a residual stock being de-oiled usually by the centrifuge method.



**White Oils and Pharmaceutical Oils.**—White oils are manufactured from suitable distillates or raffinates by a heavy treatment with fuming sulphuric acid, usually about "15–20 per cent. oleum." This treatment removes virtually all the aromatic compounds present in the oil, at the same time forming sulphonic acids.

The sulphonic acids are usually classified as either "green" or "mahogany," the difference being largely one of paraffin side chain length. The green acids, having short paraffin side chains, are water soluble, and are separated in the acid layer, while the mahogany acids, having a longer paraffin side chain, are soluble in oil, from which they must be removed by extraction with aqueous alcohol, before or after neutralisation.

The sodium salts of the "green" acids are used as wetting agents, and those of the "mahogany" acids as emulsifying agents, or as "Twitchell" reagent for fat splitting. (See p. 92.)

After the neutralisation stage the oil is washed with water to remove any remaining alkali or sulphonate, and then finally clay treated.

**Asphaltic Bitumen.**—The manufacture of bitumen may be divided into two sections:

- (1) By vacuum distillation of suitable crude oil residues, the residue from this distillation having the properties of bitumen.
- (2) Certain crude oils do not give a good quality bitumen in distillation. If the distillation residue is heated and blown with air, a good quality bitumen may then be produced. It is supposed that the process consists of direct oxidation, or oxidation followed by the removal of the reaction product water, followed again by polymerisation.

The plant used consists essentially of a heater and a tank in which the blowing takes place. The tank may hold up to 20,000 gallons of oil, the air supplied amounting to about 100 cu. ft. per minute per ton charge. As the oxidation process is exothermic, provision is usually made to dissipate the heat produced, otherwise spontaneous combustion may occur.

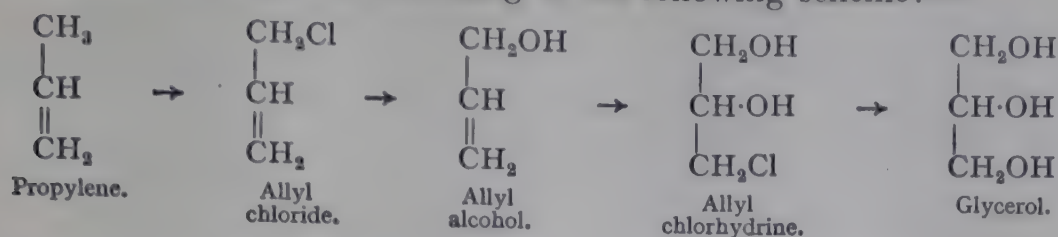
**Petroleum as a Source of Raw Materials for the Chemical Industry.**—During the last few years there has developed a considerable chemical industry based on the low molecular weight olefines produced in the various cracking processes, and formerly used as fuel.

The first manufacturing process based on these "chemical bricks," as they have been called, was a method for making *isopropyl* alcohol. In this process, the gases are first desulphurised and separated into fractions by washing with cooled gas oil, in which the  $C_4$  and higher hydrocarbons dissolve. The stripped gas, containing propylene and ethylene, is converted into *isopropyl* alcohol by solution in 93–100 per cent. sulphuric acid, the temperature of which is kept below 30° C. to prevent polymerisation. The gas oil from the scrubbers is stripped of its high olefine content in two or more stages, at different temperatures and pressures, whereby the amylenes and butylenes are separated from each other. The butylene and amylene fractions are treated with 60 per cent. sulphuric acid to convert the *isohydrocarbons* into tertiary alcohols, while a further treatment with 75–83 per cent. acid suffices to convert the unabsorbed butylenes and amylenes into secondary alcohols.

Ethyl alcohol is also produced to the extent of many million gallons per year by a similar method. Processes have been put into operation for the production of ethylene from refinery gas, a reaction favoured by temperatures of the order of 800° C. It is considerably cheaper to make ethyl alcohol from ethylene than by fermentation processes, and this also applies to all the products for which ethyl alcohol can be considered the starting point; ethers, aldehydes, ketones, acids, and so on.

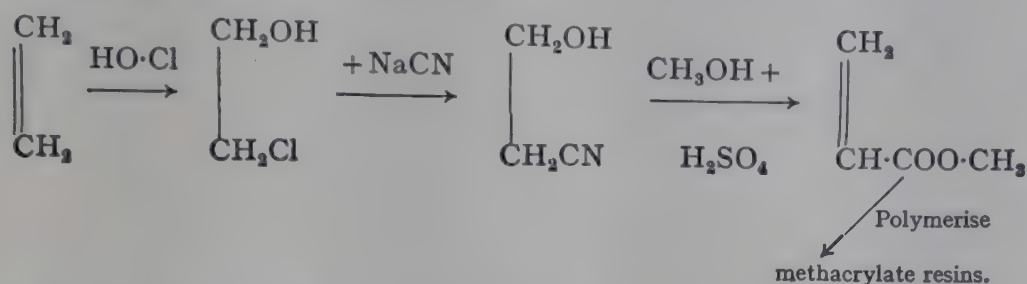


Glycerol can be prepared according to the following scheme:—



Other processes are in operation for the production of nitroparaffins, which are a source of aliphatic amines.

In the plastics field, vinyl chloride, produced from ethylene via ethylene dichloride, is the parent material for the production of polyvinyl chlorides. The acrylic resins may be made as follows:—



During both World Wars toluene was in short supply. In World War I a considerable quantity was derived from the products of vapour phase cracking, by Hall in this country and by Rittman in the U.S.A. The yields were poor, and there was considerable trouble due to coking. World War II was better served by the aromatisation processes, both hydroforming and dehydrogenation. The manufacture of toluene by either of these processes involves the extraction of the naturally occurring toluene in straight run naphtha, plus the dehydrogenation of methylcyclohexane. The toluene is recovered by extractive distillation, acid treating and caustic washing to produce a nitration grade (99 per cent. purity). In some plants a method of azeotropic distillation is used, using methyl-ethyl ketone and water to produce the azeotropes.

The Catarole process, designed for the high temperature catalytic cracking of kerosene or gas oil, is said to produce about 50 per cent. gas, of which nearly half is the  $\text{C}_2$ - $\text{C}_2$  olefines, and 50 per cent. liquids which are about 95 per cent. aromatics. It is claimed that there will be a regular production of the usual coal tar chemicals, such as benzene, toluene, ethylbenzene, styrene, xylenes, anthracene, phenanthrene, etc., which will be purified by distillation and, where necessary, crystallisation. It is also claimed that the aromatic products are more free from impurities, particularly sulphur and nitrogen compounds, than are the corresponding coal tar products. From the olefines will be made alcohols (ethyl and isopropyl), ethylene oxide, ethylene chlorhydrin, glycol, glycerine, etc.

A most convenient way of manufacturing hydrogen is by passing a mixture of refinery gas and steam over a heated catalyst. A large quantity is made available this way, and this can be used in hydrogenation processes, not only in the production of hydrocarbons, but in the hardening of fats for instance. It is also used in the production of ammonia, nitric acid, or ammonium nitrate. Such a process is already in operation in Arkansas, U.S.A. The plant is designed for the manufacture of hydrogen, ammonia, nitric acid, and ammonium nitrate, all at the same time. The nitrogen is, of course, taken from the air.

Modern methods of  $\text{H}_2\text{S}$  and mercaptan removal give the sulphur compounds in a condition from which either they can be burned to produce sulphuric acid, or alternatively, processed to produce sulphur. Already there are many refineries operating which are independent of purchased supplies of sulphuric acid.

During the War, Germany is said to have had capacity for the production of 80,000 tons per year of fatty acids from the oxidation of paraffin wax by

potassium permanganate. Synthetic butter is supposed to have been made by esterification with glycerol.

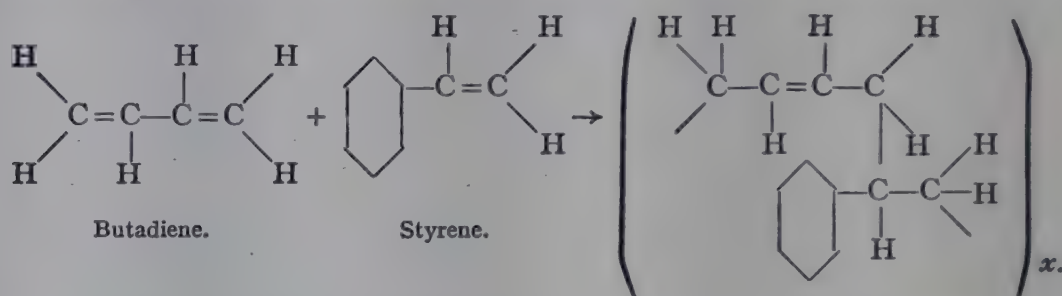
There are now many wetting compounds and detergents available from petroleum. Some of these are manufactured by the sulphonation of long chain olefines



Other products contain the long chain ethylene oxide molecules  $(\text{C}_2\text{H}_4\text{O})_n$  where  $n$  is 6 to 10. The importance of these compounds cannot be exaggerated in a world condemned to a shortage of fats for soap-making.

**Synthetic Rubber.**—The petroleum industry played a considerable rôle in the production of the 900,000 tons of synthetic rubber per year achieved in the U.S.A. by 1945.

Most of the production consisted of "G-R-S rubber," which is made by co-polymerising styrene with butadiene, which has been represented as follows:—



Butadiene, in the petroleum industry, is produced by the dehydrogenation of butane or the  $\text{C}_4$  fraction from cracked gases.

The process available consists of passing the preheated charge stock over a heated chromic oxide-alumina type catalyst, in two stages. The first step yields butane, butene, and lighter gas. The butane-butene portion is concentrated in a vapour recovery system to produce the charge for the second step, in which butadiene production is effected. After passing through the second stage, the hydrocarbon vapours are cooled, compressed and sent to a conventional vapour recovery system, where a cut of butadiene-butane-butene is obtained.

In the catalytic dehydrogenation of butenes, the principal process problem centres about the reactor. The most serious limitation in process design is the tendency for butadiene to polymerise and ultimately to degrade to coke and hydrogen. This can be minimised by operating at hydrocarbon partial pressures of the order of 90 to 100 millimetres of mercury. The low partial pressures can be obtained by low pressure operation or by the use of an inert gas as a diluent.

Difficulties in the separation of butadiene from the substances associated with it are indicated by the close boiling-points of some other  $\text{C}_4$  compounds:

<i>Compound.</i>	<i>Boiling-point °C.</i>
<i>Isobutane</i>	− 11·7
<i>Isobutene</i>	− 6·7
<i>Butene—1</i>	− 6·2
<i>Butadiene</i>	− 4·5
<i>n-Butane</i>	− 0·5
<i>Butene—2 trans.</i>	+ 1·0
<i>Butene—2 cis</i>	+ 3·7

The method used for extraction is to pass the mixture through a solution of cuprous chloride and hydrochloric acid. The butadiene forms a yellow solid compound, whereas butene, etc., remain in solution. The solid, after separation, is heated to 30°–100° C., when the butadiene is released. The other  $\text{C}_4$  hydro-



carbons are recycled back for conversion. Another method uses extractive distillation, using furfural as the extractive solvent.

Styrene is usually produced by the dehydrogenation of ethylbenzene. The ethylbenzene was first produced by the alkylation of benzene with ethylene or ethyl alcohol, using aluminium chloride as a catalyst. During the war, it was found that the catalytic polymerisation plants built for the polymerisation of olefines, using a phosphoric type catalyst, could be switched without difficulty to the ethylene/benzene reaction. The products of reaction include not only ethylbenzene, but also benzene, toluene, diethylbenzene and heavy aromatics, besides  $C_2$ - $C_5$  compounds. Separation is effected by a combination of absorption and fractionation processes.

The dehydrogenation process is the standard one of passing the heated ethylbenzene vapour with superheated steam at  $630^\circ\text{C}$ . over suitable catalysts, said to be of the bauxite type.

The average composition of the product is:

Styrene . . .	37	per cent.
Ethylbenzene . . .	61.1	„
Toluene . . .	1.1	„
Benzene . . .	0.6	„
Tar . . .	0.2	„

The boiling-points of styrene and ethylbenzene differ by only  $9^\circ\text{C}$ ., and, in addition, distillation at atmospheric pressure would result in the polymerisation of the styrene. The separation is effected by adding to the mixture a small quantity of elemental sulphur, as a polymerisation inhibitor, and fractionating at a low absolute pressure.

**G-R-S Rubber (Buna-S).**—In the manufacture of G-R-S Rubber (G-R-S = Government Rubber Styrene) which represents over 85 per cent. of the total synthetic rubber produced, butadiene and styrene in the ratio of 3 to 1 are charged to the reactors, glass- or enamel-lined vessels of about 4000 gallons capacity, together with a catalyst, chain modifier, soap solution and water. The mixture is heated and agitated to start polymerisation, although once polymerisation is under way the reaction is exothermic and the excess heat must be removed. The co-polymer which results forms an emulsion called “latex,” and is similar to natural rubber latex.

The usual practice is to carry the reaction to only about 75 per cent. completion, this being considered the most efficient stopping point. As a result, the latex discharged from the reactors contains unreacted butadiene and styrene, which are removed and recovered. Butadiene is removed in flash tanks, after which the styrene is removed from the latex by stripping with steam. The recovered butadiene and styrene are condensed for re-use, and the stripped latex coagulated.

**Buna-N or Perbunan Rubber.**—If acrylonitrile instead of styrene is used with butadiene, Buna-N is produced. This rubber has the great advantage of swelling only very slightly when immersed in oil. This rubber was used to a large extent for self-sealing petrol tanks, pipe lines, etc.

**Butyl Rubber.**—This type of rubber was an American development. Its constituents are 98 per cent. *isobutene* and 2 per cent. *isoprene*, both of which are obtained from refinery gas. (These proportions are varied slightly for different uses.)

The *isobutene* and *isoprene* are mixed together with a diluent in tanks, from which the material is fed continuously to the reactors. Before being introduced to the reactors it is chilled to  $-100^\circ\text{C}$ ., using first ammonia and then ethylene as a refrigerant. The feed stock and catalyst are introduced continuously into the reactor, and sufficient agitation is provided to make a thin slurry.

The products of the polymerisation reaction, which include butyl rubber polymer, unreacted isobutene and diluent, flow into flash drums at 65° C., to vaporise the unreacted *isobutene* and diluent, and to destroy any remaining catalyst. Water is added, the butyl polymer stripped to remove the last traces of diluent, and the rubber is ready for coagulation.

Butyl rubber is much more impermeable to air than any other kind of rubber and is extensively used for the manufacture of inner tubes.

In August 1944, Colonel Bradley Dewey resigned from the office of Rubber Director of the United States. His work was complete, and in his farewell message he said, "I cannot see any capitalist planting rubber trees and waiting seven years for them to grow, against a future of unknown labour costs, in competition with chemists who have won every battle they ever entered between synthetics and nature."



### III.—THE MANUFACTURE, AND PROPERTIES AND USES OF ANIMAL AND VEGETABLE OILS, FATS, AND WAXES, INCLUDING LINSEED OIL; AND THE MANUFACTURE OF VARNISHES, ENAMELS, OILCLOTH, AND LINOLEUM

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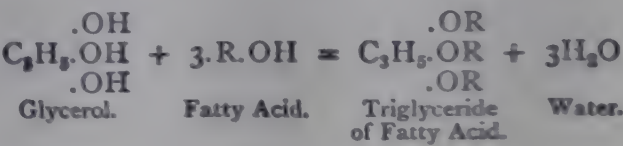
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#### INTRODUCTION

Fats and fatty oils occur disseminated throughout the tissues of almost all animals and seeds in the form of minute globules enclosed within a thin skin, forming a reserve food for the organism. Pressure alone will not usually suffice to break up the animal fat cells; the tissue must be heated when it shrivels up as it loses water, while the increasing temperature causes the fat globules to expand, burst the cell, and flow out as a liquid mass. In the case of vegetable seeds pressure alone often secures the expulsion of the oil although here, too the operation is much facilitated by a gentle heat.

The difference between a fatty oil and a fat is merely one of physical condition due to temperature; an oil freezes into a fat, and a fat melts to an oil. In a warm climate a substance will always appear as an "oil," whereas the same body will appear to the inhabitants of a colder clime as a solid fat. Thus, for example, cocoanut oil is liquid in India but solid in England, where it is used by vegetarians in place of butter. As previously explained, "mineral" oils are quite different in chemical character to a vegetable or animal oil.

Chemically considered, fats and fatty oils are bodies produced by the chemical union of glycerol with fatty acids. *Glycerol* is a trihydric alcohol, of formula  $C_3H_5(OH)_3$ . It is capable of combining with three molecules of fatty acids to form "triglycerides," thus :—



Where R stands for the radicle of the fatty acid.

Fats and fatty oils are merely mixtures of these triglycerides of the fatty acids. The three glycerides which usually predominate in most fats are solid tristearin, solid tripalmitin, and liquid triolein—the respective glycerides of stearic, palmitic, and oleic acids. Solid fats usually contain much stearin and palmitin, but little olein; liquid fats, on the other hand, consist principally of olein. Other fats and oils exist (*e.g.*, linseed and castor oils) which are composed of glycerides of other acids than those mentioned above. We append a list of the principal fatty acids occurring in natural fats and oils, together with the names and formulæ of their triglycerides.

FATTY ACIDS AND THEIR TRIGLYCERIDES

Saturated Acids of the Acetic Series.  $C_nH_{2n+1}.COOH$ .

Acid.	Formula.	M. P. (° C.)	B. P. (° C.)	Corresponding Glyceride.	Formula.
Formic -	H.CO <sub>2</sub> H	8.3	101	Formin -	C <sub>3</sub> H <sub>5</sub> (O.HCO) <sub>3</sub>
Acetic -	CH <sub>3</sub> .CO <sub>2</sub> H	16.5	118	Acetin -	C <sub>3</sub> H <sub>5</sub> (O.CH <sub>3</sub> CO) <sub>3</sub>
Propionic -	C <sub>2</sub> H <sub>5</sub> .CO <sub>2</sub> H	- 22.0	141	Propionin -	C <sub>3</sub> H <sub>5</sub> (O.C <sub>2</sub> H <sub>5</sub> CO) <sub>3</sub>
Butyric	C <sub>3</sub> H <sub>7</sub> .CO <sub>2</sub> H	- 7.9	162	Butyrin -	C <sub>3</sub> H <sub>5</sub> (O.C <sub>3</sub> H <sub>7</sub> CO) <sub>3</sub>
(normal iso)		- 79.0	154		
Valeric	C <sub>4</sub> H <sub>9</sub> .CO <sub>2</sub> H	- 58.5	185	Valerin -	C <sub>3</sub> H <sub>5</sub> (O.C <sub>4</sub> H <sub>9</sub> CO) <sub>3</sub>
(normal iso)		- 51.0	174		
Caproic -	C <sub>5</sub> H <sub>11</sub> .CO <sub>2</sub> H	- 8.0	205	Caproin -	C <sub>3</sub> H <sub>5</sub> (O.C <sub>5</sub> H <sub>11</sub> CO) <sub>3</sub>
Aethanthylic -	C <sub>6</sub> H <sub>13</sub> .CO <sub>2</sub> H	- 10.0	223	Aethanthylin -	C <sub>3</sub> H <sub>5</sub> (O.C <sub>6</sub> H <sub>13</sub> CO) <sub>3</sub>
Caprylic -	C <sub>7</sub> H <sub>15</sub> .CO <sub>2</sub> H	16.5	237.5	Caprylin -	C <sub>3</sub> H <sub>5</sub> (O.C <sub>7</sub> H <sub>15</sub> CO) <sub>3</sub>
Perlargonic -	C <sub>8</sub> H <sub>17</sub> .CO <sub>2</sub> H	12.5	186	Perlargonin -	C <sub>3</sub> H <sub>5</sub> (O.C <sub>8</sub> H <sub>17</sub> CO) <sub>3</sub>
Capric -	C <sub>9</sub> H <sub>19</sub> .CO <sub>2</sub> H	31.3	200	Caprin -	C <sub>3</sub> H <sub>5</sub> (O.C <sub>9</sub> H <sub>19</sub> CO) <sub>3</sub>
Undecylic -	C <sub>10</sub> H <sub>21</sub> .CO <sub>2</sub> H	28.0	212	Undecylin -	C <sub>3</sub> H <sub>5</sub> (O.C <sub>10</sub> H <sub>21</sub> CO) <sub>3</sub>
Lauric -	C <sub>11</sub> H <sub>23</sub> .CO <sub>2</sub> H	43.6	225	Laurin -	C <sub>3</sub> H <sub>5</sub> (O.C <sub>11</sub> H <sub>23</sub> CO) <sub>3</sub>
Tridecylic -	C <sub>12</sub> H <sub>25</sub> .CO <sub>2</sub> H	40.5	236	Tridecylin -	C <sub>3</sub> H <sub>5</sub> (O.C <sub>12</sub> H <sub>25</sub> CO) <sub>3</sub>
Myristic -	C <sub>13</sub> H <sub>27</sub> .CO <sub>2</sub> H	53.8	248	Myristin -	C <sub>3</sub> H <sub>5</sub> (O.C <sub>13</sub> H <sub>27</sub> CO) <sub>3</sub>
Pentadecatoic -	C <sub>14</sub> H <sub>29</sub> .CO <sub>2</sub> H	51.0	257	Pentadecatoin -	C <sub>3</sub> H <sub>5</sub> (O.C <sub>14</sub> H <sub>29</sub> CO) <sub>3</sub>
Palmitic -	C <sub>15</sub> H <sub>31</sub> .CO <sub>2</sub> H	62.0	268	Palmitin -	C <sub>3</sub> H <sub>5</sub> (O.C <sub>15</sub> H <sub>31</sub> CO) <sub>3</sub>
Margaric -	C <sub>16</sub> H <sub>33</sub> .CO <sub>2</sub> H	60.0	277	Daturin -	C <sub>3</sub> H <sub>5</sub> (O.C <sub>16</sub> H <sub>33</sub> CO) <sub>3</sub>
Stearic -	C <sub>17</sub> H <sub>35</sub> .CO <sub>2</sub> H	69.3	287	Stearin -	C <sub>3</sub> H <sub>5</sub> (O.C <sub>17</sub> H <sub>35</sub> CO) <sub>3</sub>
Nondecylic -	C <sub>18</sub> H <sub>37</sub> .CO <sub>2</sub> H	66.5	298	Nondecylin -	C <sub>3</sub> H <sub>5</sub> (O.C <sub>18</sub> H <sub>37</sub> CO) <sub>3</sub>
Arachidic -	C <sub>19</sub> H <sub>39</sub> .CO <sub>2</sub> H	77.0	...	Arachidin -	C <sub>3</sub> H <sub>5</sub> (O.C <sub>19</sub> H <sub>39</sub> CO) <sub>3</sub>
Medullic -	C <sub>20</sub> H <sub>41</sub> .CO <sub>2</sub> H	...	...	Medullin -	C <sub>3</sub> H <sub>5</sub> (O.C <sub>20</sub> H <sub>41</sub> CO) <sub>3</sub>
Behenic -	C <sub>21</sub> H <sub>43</sub> .CO <sub>2</sub> H	83.0	306 (60 mm.)	Behenin -	C <sub>3</sub> H <sub>5</sub> (O.C <sub>21</sub> H <sub>43</sub> CO) <sub>3</sub>
Carnaubic -	C <sub>22</sub> H <sub>45</sub> .CO <sub>2</sub> H	72.5	...	...	...
Hyaenic -	C <sub>24</sub> H <sub>49</sub> .CO <sub>2</sub> H	77.5	...	...	...
Cerotic -	C <sub>26</sub> H <sub>53</sub> .CO <sub>2</sub> H	78.0	...	...	...
Melissic -	C <sub>29</sub> H <sub>59</sub> .CO <sub>2</sub> H	91.0	...	...	...



FATTY ACIDS AND THEIR TRIGLYCERIDES—*continued**Unsaturated Fatty Acids of the Oleic Series.*  $C_nH_{2n-1}COOH$ .

Acid.	Formula.	M.P. (° C.)	B.P. (° C.)	Correspond- ing Glyceride.	Formula.
Acrylic -	$C_3H_3\cdot COOH$	+13	140	...	...
Crotonic -	$C_4H_5\cdot COOH$	71.5	180.5	...	...
Iso-crotonic -	$C_4H_5\cdot COOH$	15.5	169	...	...
Angelica -	$C_5H_7\cdot COOH$	45	185	...	...
Tiglic -	$C_5H_7\cdot COOH$	65	198	...	...
Hypogaeic -	$C_{15}H_{29}\cdot COOH$	...	...	...	$C_3H_5(O\cdot C_{15}H_{29}CO)_3$
Oleic -	$C_{17}H_{33}\cdot COOH$	14 {	223 (10 mm.) 250 (super- heated steam)	Olein -	$C_3H_5(O\cdot C_{17}H_{33}CO)_3$

*Unsaturated Fatty Acids of the Linolic Series.*  $C_nH_{2n-3}COOH$ .

Elaeostearic - (Elaeomargaric)	} $C_{16}H_{29}\cdot COOH$	43	...	Elaeostearin	$C_3H_5(O\cdot C_{16}H_{29}CO)_3$
Linolic -		$C_{17}H_{31}\cdot COOH$ { below - 18 }	...	Linolein -	$C_3H_5(O\cdot C_{17}H_{31}CO)_3$

*Unsaturated Fatty Acids of the Linolenic Series.*  $C_nH_{2n-5}COOH$ .

Linolenic -	$C_{17}H_{29}\cdot COOH$	Liquid	...	Linolenin -	$C_3H_5(O\cdot C_{17}H_{29}CO)_3$
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*Unsaturated Fatty Acids of the Recinoleic Series.*

Recinoleic -	$C_{17}H_{32}(OH)\cdot COOH$	4	...	Recinolein -	$C_3H_5(O\cdot C_{17}H_{32}(OH)\cdot CO)_3$
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It may be noticed that monoglycerides and diglycerides, corresponding to the formulæ  $C_3H_5\cdot OH$  and  $C_3H_5\cdot OR$ , exist in rancid or partially hydrolysed fats, while mixed glycerides of the

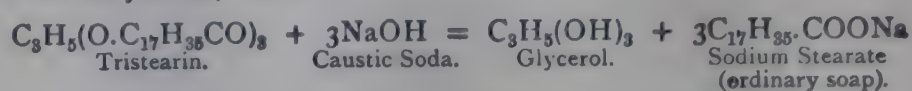
formula  $C_3H_5\cdot OR_1$  ( $R_1, R_2, R_3$ , corresponding to three different acid radicles) certainly occur in small quantities in certain normal fats, *e.g.*, in ordinary butter-fat, also in tallow.

Fats are usually neutral bodies, but old or rancid fats often contain large quantities of free fatty acids, which may be extracted by sodium carbonate solution or by alcohol. Old palm oil, and some fish oils, often contain no less than 60 per cent. of free fatty acids.

While at ordinary temperatures some fats are white crystalline solids, others are fluids, fatty to the touch; all produce permanent grease-spots on paper; they are insoluble in water, slightly soluble in alcohol, easily soluble in ether, benzene, chloroform, carbon disulphide, and carbon tetrachloride. When distilled alone they decompose, producing vapours of acrolein; with high tension steam they distil with partial saponification into free acids and glycerol.

Pure fats are tasteless, odourless, and keep for years. When, however, they contain small quantities of nitrogenous animal or vegetable impurities they often turn rancid in the presence of air, decomposing into free acids and glycerol by a process of enzyme hydrolysis. Oxygen is absorbed during this change, and the acids formed are often oxidised to oxyacids, while the glycerol is also partially destroyed. In air-tight vessels, in the absence of oxygen, fats do not become rancid.

When heated with an aqueous (but best with an alcoholic) solution of sodium or potassium hydroxide fats are completely "saponified" into glycerol and the alkali salt of the fatty acid, thus:—

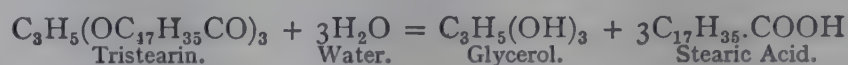


The metallic or inorganic salts of the fatty acids are called "soaps."

Other bases, such as slaked lime, magnesia, and lead oxides, readily saponify most fats, the resultant soaps, however, being usually insoluble.

It should be particularly noticed that the alkali carbonates, such as sodium or potassium carbonates, will not saponify fats even when boiled with them at ordinary pressures. Heated under high pressure in autoclaves they readily saponify (see p. 108).

Superheated steam or hot acids "hydrolyse" fats into glycerol and free fatty acids, thus:—



Certain ferments present in seeds (especially in castor seeds) readily split fats into glycerol and fatty acids at ordinary temperatures. See under *Candles*, p. 92.

The fats and fatty oils are used for making soap, candles, lubricants, varnishes, paints, for burning in lamps, and for edible purposes. The industry is an enormous one.

Fats have been artificially synthesised.

**Synthetic Fatty Acids and Fats.**—Fats are now produced synthetically by the oxidation of Fischer Tropsch hydrocarbons to acids at 100° C. in a current of air in the presence of manganese salts as catalysts. After about 24 hours the material contains 30–40 per cent. acids, which are removed by soda solution under high pressure at 200° C., and the unchanged hydrocarbons resubmitted to the process. Acids from low molecular weight to those containing 20 carbon atoms are obtained. These acids are distilled and those suitable for soap manufacture are separated. They have the disadvantage of pronounced odour and cannot compete with those from natural sources for price and purity. It is interesting to note that edible products by esterification of these fatty acids with glycerol have been obtained. These are odourless, as the low molecular weight fatty acids produce odourless glycerides.

**Synthesis of Oils and Fats in the Plant and Animal.**—The primary seat of the production of fats is the vegetable kingdom. In plants the carbon dioxide that they consume is converted into carbohydrate by combination with water in the presence of chlorophyll and sunlight, which in turn is converted into fatty compounds by the presence of enzymes and sunlight. This latter transformation takes place mainly when the fruit ripens and the fat occurs in the endosperm. The purpose in nature of these fats is to nourish the seed during germination when the fat is reconverted into sugar-like compounds once more.

In animals, fats are produced directly from the assimilation of the endosperm of plants and also by vital synthesis from other types of organic matter, such as carbohydrates and proteins.

Broadly speaking, fats fall into two classes; those with unsaturated fatty acids and those with saturated fatty acids. Two examples are oleic acid (unsaturated),  $\text{CH}_3\text{—}[\text{CH}_2]_7\text{—CH=CH—}[\text{CH}_2]_7\text{—COOH}$ , and palmitic acid (saturated),  $[\text{CH}_3\text{CH}_2]_{14}\text{COOH}$ . Both these and nearly all other fatty acids are straight chain aliphatic acids. There are very few branched-chain fatty acids.

Some specific points about a few fats follow:—

*n*-butyric acid glycerides are contained in quantities up to 10 per cent. in milk fats, but do not occur in any other natural fat. Other fats in milk are the glycerides of *n*-caproic, *n*-caprylic and *n*-capric acids which are found in much larger proportions in coconut and palm-kernel oils.

*n*-lauric acid occurs abundantly in coconut and palm-kernel oils, and also comprises 20 per cent. of sperm whale oil. The sodium salt is used for soap manufacture as it forms an abundant lather.

*n*-myristic acid occurs in considerable proportion in the nutmeg family and also very widely in other oils, but in smaller proportions (5–10 per cent. in whale and fish oils).

*n*-palmitic acid is the most abundant of the natural saturated fatty acids. It is contained in the glycerides of butter fat, palm oil, cacao butter, tallow and other oils to the extent of 20–30 per cent. In groundnut oils, linseed, olive and soya bean it is present to 3–10 per cent. Palmitic acid is used together with stearic acid in candles.

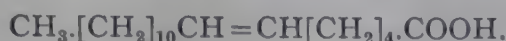
*n*-stearic acid is present in nearly all natural fats in a proportion of about 1–5 per cent. In lards and tallow *n*-stearic acid forms 10–30 per cent. of the fatty acids present,



Unsaturated fatty acids are of wider importance in industry than the saturated acids. Oleic acid, for example, is largely used in soaps and gives a good lather. Linseed oil has very wide uses in paint, linoleum, and wherever a drying oil is required. Linseed oil owes its drying properties to the presence of the glycerides of the unsaturated linoleic and linolenic acids. Olein (the glyceride of oleic acid), *e.g.*, rape seed oil and neat's foot oil, is unsaturated but fairly mobile, while castor oil (the glyceride of ricinoleic acid) is viscous but also unsaturated (one double bond).

Nearly all the unsaturated acids found in nature are straight chain acids which may be converted into saturated acids by hydrogenation and thus identified. With unsaturated acids, the position of the double bond may vary, *e.g.*, with oleic acid.

$\text{CH}_3\text{.}[\text{CH}_2]_7\text{.CH=CH.}[\text{CH}_2]_7\text{.COOH}$  is the most abundant form of oleic acid, while petroselenic acid, the glyceride of which forms the main constituent of parsley-seed oil, has the formula



Linoleic acid,  $\text{CH}_3[\text{CH}_2]_4\text{.CH=CH.CH}_2\text{.CH=CH}[\text{CH}_2]_7\text{.COOH}$ , is more unsaturated than oleic, and is a drying oil. Oxygen adds on at the double bonds (see p. 46-47, on Drying of Oils). Linolenic acid has three double bonds,  $\text{CH}_3\text{.CH}_2\text{.CH=CH.CH}_2\text{.CH=CH.CH}_2\text{.CH=CH.}[\text{CH}_2]_3\text{.COOH}$ .

Ricinoleic acid is a typical example of the hydroxylated fatty acids. Its formula is  $\text{CH}_3\text{.}[\text{CH}_2]_5\text{.CH(OH).CH}_2\text{.CH=CH.}[\text{CH}_2]_7\text{.COOH}$ . Castor oil contains glycerol triricinoleate. This is practically the only trihydroxylated glyceride. Ricinoleic acid forms an internal anhydride—an estolide—on heating. The hydroxyl group is usually protected by acetylation when estolides are undesirable.

**The Alcoholic Constituents of Fats and Waxes.**—There are three principal alcohols in natural fats and waxes: glycerol,  $\text{CH}_2\text{.OH.CH(OH).CH}_2\text{.OH}$ , in fats; trimethylene glycol,  $\text{CH}_2\text{OH.CH}_2\text{.CH}_2\text{OH}$ , formed during fermentation when reducing conditions are present; and aliphatic alcohols from  $\text{C}_{12}$  to  $\text{C}_{30}$ , together with minute quantities of sterols (in wool fat and liver oils).

Glycerol is fully treated in another section. Trimethylene glycol is produced during fermenting decay of fats. Its presence in glycerol for the explosives industry is very undesirable and care is taken to avoid this.

Some of the aliphatic alcohols present in waxes are shown in the following table with some of their properties:—

Name of Alcohol.	Formula.	Melting point.	Boiling point.	Melting point of Acetate.
Hexadecyl alcohol † (cetyl alcohol) .	$\text{C}_{16}\text{H}_{33}\text{.OH}$	50° C.	151° C. (2 m.m.)	23° C.
Octadecyl alcohol † .	$\text{C}_{18}\text{H}_{37}\text{.OH}$	59° C.	...	31° C.
Eicosyl alcohol † .	$\text{C}_{20}\text{H}_{41}\text{.OH}$	71° C.	...	44° C.
Hexacosyl alcohol † .	$\text{C}_{26}\text{H}_{53}\text{.OH}$	79.5° C.	...	65° C.
Triacontanlyl † .	$\text{C}_{30}\text{H}_{61}\text{.OH}$	86.5° C.	...	75° C.
Hexadecenyl alcohol *	$\text{C}_{16}\text{H}_{31}\text{.OH}$	Liquid.	153° (2 m.m.)	...
Octadecenyl alcohols *	$\text{C}_{18}\text{H}_{35}\text{.OH}$	Liquid.	...	...
Eicosenyl alcohols *	$\text{C}_{20}\text{H}_{39}\text{.OH}$	Liquid.	...	...

\* Unsaturated.

† Saturated.

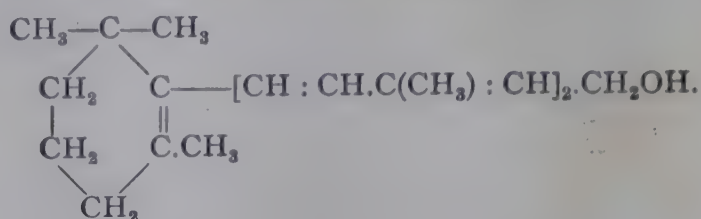
Esters of cetyl alcohol with lauric, myristic and palmitic acids occur in the head of the sperm whale. Octadecyl alcohol is present as esters to an even greater extent.

**Sterols.**—These are alcohols of considerable biochemical significance. They constantly accompany fats and waxes whether these be of animal or vegetable origin. Cholesterol is the most important and abundant sterol of animal origin. Its formula is  $\text{C}_{27}\text{H}_{45}(\text{OH})$ . This is found in large quantities in wool fat, and in the skin of all animals in small quantities. It is optically active ( $\alpha_D - 35^\circ$ ), has a m.p. of  $148.5^\circ\text{C}$ ., and the acetate melts at  $114^\circ\text{C}$ . The rotation of acetate is  $-42^\circ$ . Cholesterol gives a violet to green coloration in the Liebermann Burchard test.

The animal sterols are known as zoosterols, while those sterols found in the vegetable kingdom are known as phytosterols, the most widely distributed of the latter being the sitosterols,  $\text{C}_{29}\text{H}_{49}(\text{OH})$ .

Vitamins A and D are contained in the unsaponifiable matter of many fats, especially in fish liver oils (*e.g.*, cod liver oil, halibut liver oil).

Vitamin A is an unsaturated alcohol with the formula:



It is closely related to carotene in formula, and carotene may actually be converted into vitamin A under suitable conditions.

For modern statistics see Appendix III.

### Manufacture of Animal Oils and Fats

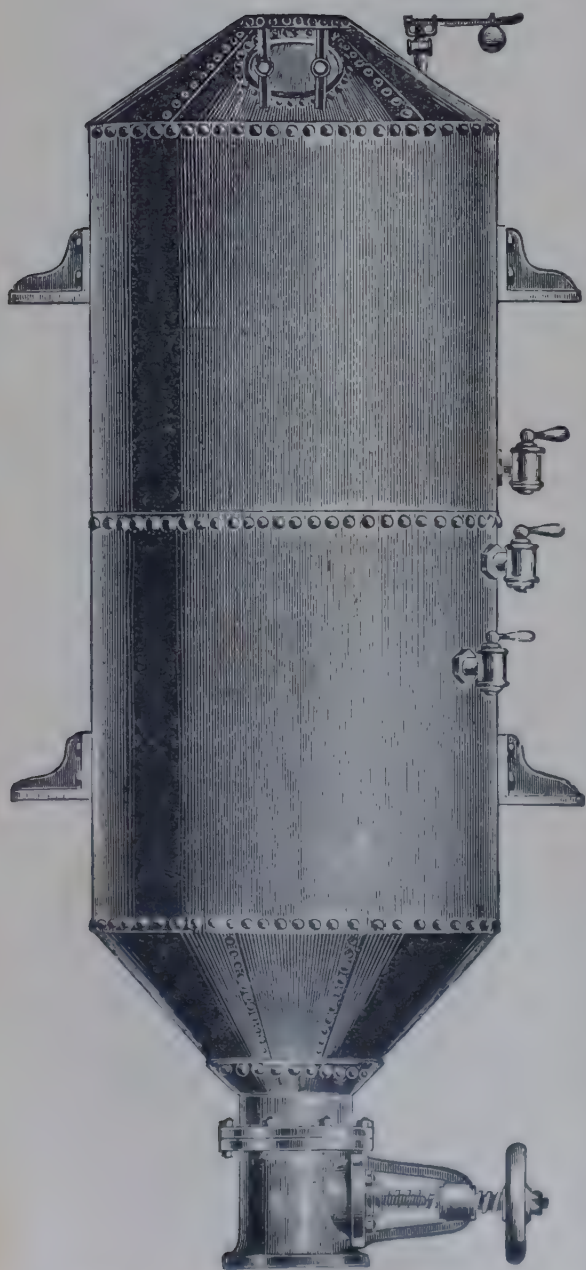


FIG. 6.—Packer's Rendering Tank.

These are usually obtained by heating the tissues rich in oil or fat, so as to cause the bursting of the fat-containing cell.

**Tallow** (beef or mutton fat).—The “rough fat” fresh from the slaughter-house is placed in a lead-lined tank provided with a steam coil for heating, and an outlet passing to a chimney stack for the escape of offensive vapours. Hot water is poured on to the fat, and the vessel and its contents heated for some hours by the steam coil. On settling, the melted fat rises to the surface as a clear layer, and is drawn off through outlet taps into another vessel. The fat is now ready for use, unless when made from inferior materials, when it must be refined and bleached as described below.

The residue of fatty matter left in the tank is acidified with a little sulphuric acid, and steam again turned on. The small amount of sulphuric acid does not hydrolyse the fats, but partially destroys the cell membranes, thus setting free their occluded fat, which is run off as before into another vessel. An inferior variety of fat is thus obtained.

Tallow for **soap making** (but not for comestible purposes) is rendered in digesters under pressure. Fig. 6 shows one of the large modern rendering tanks used in the American packing industry; made of riveted steel plates and capable of standing a working pressure of four or five atmospheres, the largest ones are 8 ft. in diameter and 20 ft. high. They are provided with safety-valves, and discharge through a gate valve at the bottom. The tank is filled to within a foot of the junction



of the upper cone and the cylindrical portion of the vessel—the material (in Chicago) often consisting of putrid carcasses of animals which have died in transit, diseased flesh, and other waste products unfit for comestible products. Then live steam at 40-50 lbs. pressure is turned on, and the contents of the boiler heated for eight to ten hours or so, the internal temperature being maintained at  $130^{\circ}$ - $140^{\circ}$  C. Two air-cocks carry away the offensive fumes evolved during the heating. Finally the steam is turned off, the vent-pipes opened to allow the steam in the tanks to blow off, and the fat is allowed to settle. The clear liquid fat floating on the surface of the water in the tank is now drawn off through the top draw-off cock, and, as the level in the tank subsides, through the lower ones in succession. Finally, water is pumped in from below, so as to raise the level of the fat (which, of course, floats upon the water) so that it too may be withdrawn through the stopcocks.

Last of all the valve at the bottom of the tank is opened, and the contents run out into a series of settling tanks and catch basins to retain fat globules still in the water. A sludge settles at the bottom of these tanks; it is drawn off and pressed. The liquid running from the tanks flows into evaporators (vacuum, triple effect)

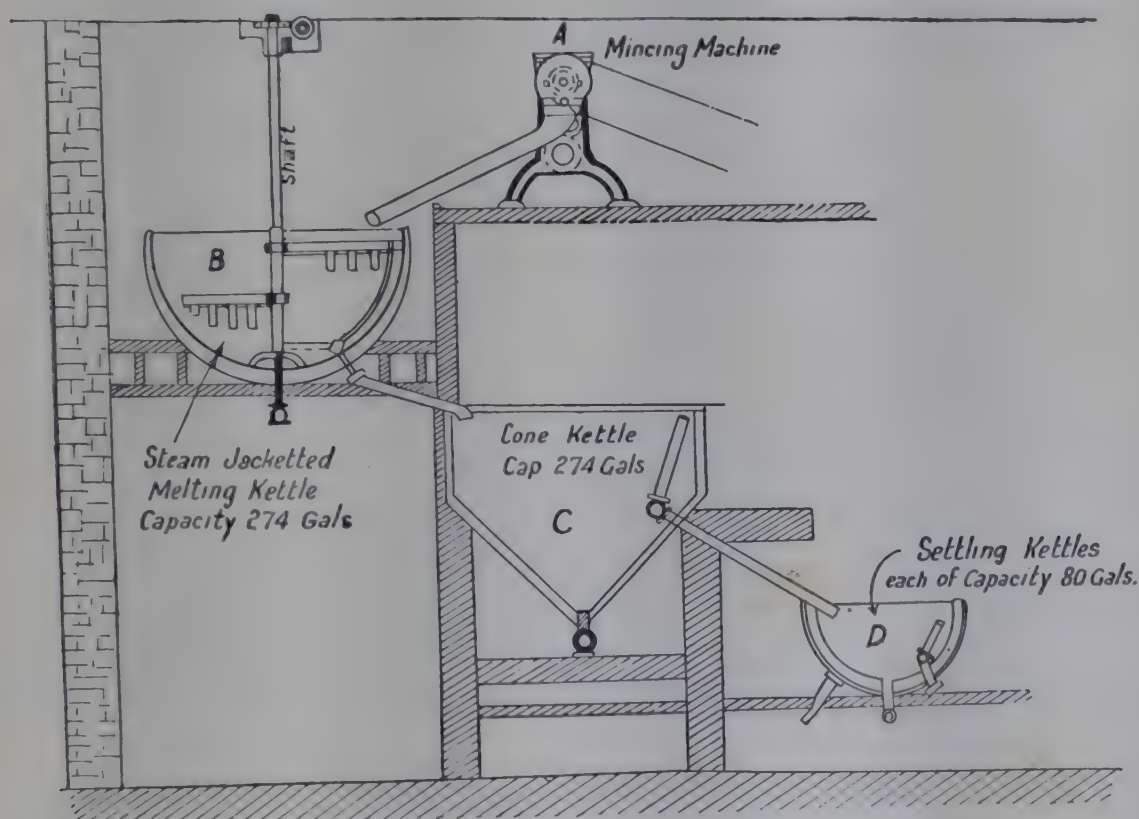


FIG. 7.—Manufacture of Oleo Stearin and Oleo Oil from Beef Fat.

where it is boiled down into a thick "soup." The sludge press-cakes are now mixed with this, and the mass sold as "Tankage Fertiliser."

**Lard** is the fat of the hog, which is separated from the slaughtered animal, and worked up as described above.

### Manufacture of Oleo Stearin and Oleo Oil from Beef Fat

The fat from the recently slaughtered animal is rapidly removed and plunged into a vat, and washed with warm water until free from blood and other impurities, hardened by immersion in ice water, chopped into a fine mass by a machine A (Fig. 7), and melted at  $70^{\circ}$ - $75^{\circ}$  C. in a steam-jacketed pan B, provided with slowly moving mechanical agitators. The mass is allowed to settle, salt being strewn over the surface of the liquid in order to accelerate the settling out of membranes and connective tissue (which collect at the bottom). Next the clear oil is siphoned over to another series of melting kettles, C, usually situated on a lower floor. More salt



is added, and the temperature maintained at  $70^{\circ}$ - $80^{\circ}$  C. until a second settling is complete. The fat, now free from membrane and connective tissue, is siphoned into shallow settling tanks and allowed to stand three to five days at a temperature (peculiar to each fat) which experience shows is best suited for allowing the stearin to crystallise. This stearin forms a crust over the surface, and the rest settles at the bottom, leaving a clear oil between. The crystallisation completed, the crust is broken into fine fragments by vigorous mechanical stirring, and the pasty mass thus obtained conveyed to a revolving table surrounded by skilled workmen, who wrap the mixture into small packages in canvas cloth (each containing about 3 lbs. weight), place them in hydraulic presses, and separate the oleo oil by great pressure slowly applied. The oil flows from the presses into large receiving tanks, while the solid stearin remains in the press as a cake, which is mixed with cotton-seed oil, and used for making lard substitute. The oleo oil is converted into margarine as described on p. 85. Caul fat yields about 50 per cent. oleo oil and 30 per cent. solid stearin, the precise yield varying considerably according to the temperature of pressing, the amount of tissue, and the quality of fat.

**Lard Stearin and Lard Oil** are obtained by treating hog fat (lard) as above described. The oil is used for illuminating purposes, and the stearin for the manufacture of lard compound and soap.

**Fat from Garbage.**—In large cities a considerable quantity of fat for soap-making is made by heating sewage or garbage in upright steel tanks of 6 tons capacity with live steam at 30 lbs. pressure for six to eight hours. The mass is run into vats, allowed to settle, and the free water and grease floating on it are run off by drop-pipes into separating tanks. The sludge is filtered through cloth, and the cakes of solid matter compressed and sold as manure.

**Fish Oils** are obtained from all parts of the body of common fish—such as sardine, salmon, sprat, herring, menhaden, etc., by boiling. The best sorts of **Cod Liver Oil** are prepared by heating the livers (taken from the fish brought ashore alive and treated the same day) of the cod fish in steam-jacketed vessels, when the cell membranes burst and the oil exudes. Inferior qualities are obtained by treating the putrid livers in a similar way; although unfit for medicinal purposes it is largely used in the leather industry (see Dégras). **Seal and whale oil** are extracted from the blubber of the animals, sometimes on board ship itself, but more often in “trying” stations situated in Finnmarken, on the Lofotes, and in Iceland. The blubber is stripped clean from the flesh immediately after the arrival of the ship, cut into strips, chopped in mincing machines, delivered into melting pans, and boiled with steam.

**Menhaden Oil** is prepared from the heads and intestines of fish, especially of the menhaden or mossbanker of the Atlantic coast of America; used in the leather, paint, and rope trades.

For **Sperm and Arctic Sperm Oil** see under **Liquid Waxes**.

### Manufacture of Vegetable Oils

Vegetable oils and fats are obtained from oil-bearing substances (usually seeds) by two distinct processes: \*—

- (a) By pressing in hydraulic presses.
- (b) By extracting with volatile solvents.

#### (a) OIL EXTRACTION BY PRESSURE

Four distinct operations are usually performed:—

(1) The seed is crushed or ground in special machines so as to break the oil cells.

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\* For blocks and illustrations of machinery employed in seed-crushing, the authors have pleasure in thanking Messrs Rose, Downs, & Thompson, of Hull.



(2) The ground seed is heated so as to facilitate the flow of oil and to coagulate the albumen.

(3) The product is now gently pressed in a moulding machine to prepare it for the hydraulic press.

(4) Finally, the seed is conveyed to hydraulic presses and the oil expressed.

Two different sorts of presses are used, viz., the Anglo-American (plate) and the cage or "cylinder" (clodding) presses. In the Anglo-American system (Fig. 8) the moulded seeds are wrapped in cloth bags and placed between a series of plates. The expressed oil runs down, and is collected in tanks below the press. In the "cage" system (Fig. 9) the seeds are confined in a closed chamber perforated with little holes, large enough to allow the oil to flow out, but small enough to retain the seed. The pressure being applied, the oil is forced out. The advantages of the latter system are:—

(1) Very great pressures can be applied, so that nearly all the oil is extracted at a single pressing.

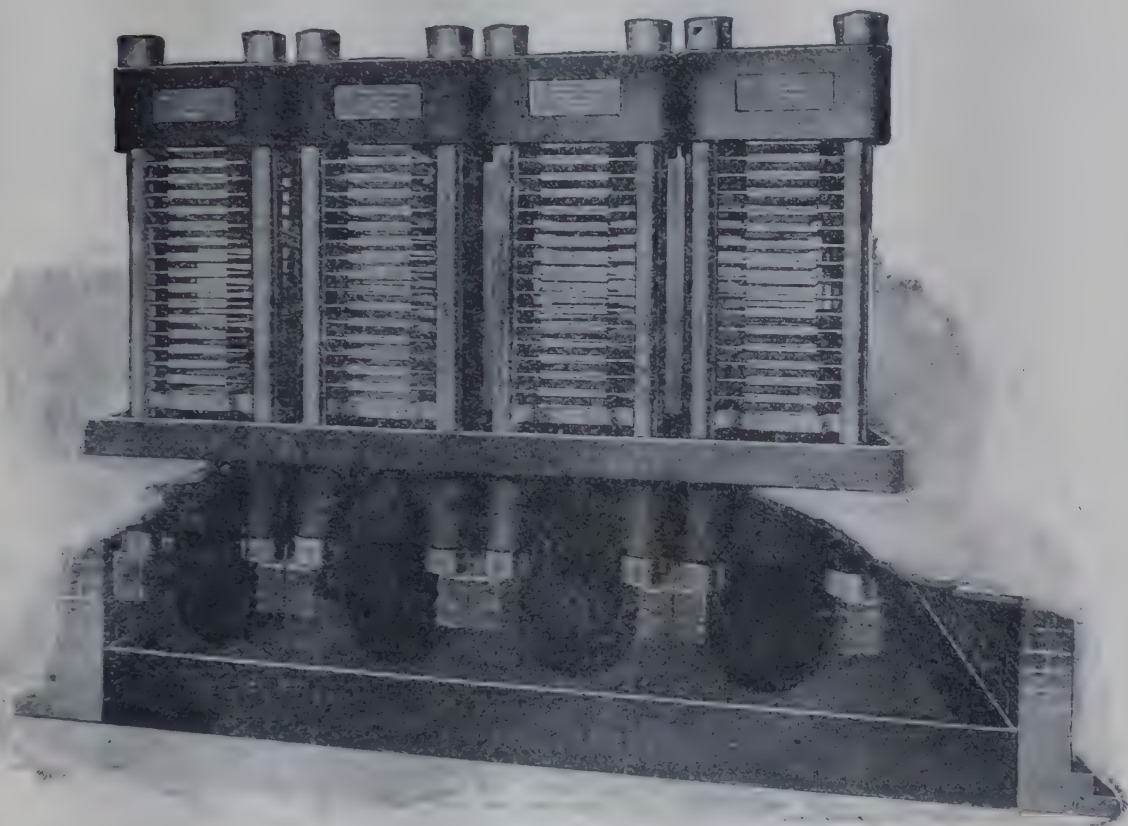


FIG. 8.—Battery of Four Anglo-American Oil Presses, having a continuous gutter for collecting the expressed oil. (Rose, Downs, & Thompson, of Hull.)

(2) No exudation of the mass from the edges of the cloths or bags occurs as in the Anglo-American system.

(3) The press cakes need not be "pared."

The plate or Anglo-American system is usually employed for the treatment of seeds requiring one pressing. A combination of both systems is often employed for very oily seeds requiring two pressings, or for the production of two qualities of oil.

Different seeds require a somewhat different treatment; linseed and cotton seed, for example, require one crushing, while castor seed and copra (the flesh of the cocoa-nut) are usually crushed twice. We will outline the process usually employed in the case of the more important seeds.

**Linseed.**—The seed must be perfectly clean. It was formerly always necessary to pass it through a screening machine to remove impurities; but now much of the linseed on the market is sold on the basis of 95 per cent. purity, and some at

97 per cent. ; such seed is ready for immediate use without further cleaning. The clean seed is now passed to the rolls or crushing machinery *c* (Fig. 10, which represents a complete oil mill designed by Rose, Downs, & Thompson, of Hull). The seed is passed into the hopper in the usual manner, and is distributed to the crushing rolls (made of hardened chilled iron) by a fluted feed roller of the same length as the crushing rolls placed at the bottom of the hopper. The feed of the



FIG. 9.—Cage or Circular Box (Clodding) Oil Press.  
(Rose, Downs, & Thompson, Hull.)

seed to the rolls can be altered at pleasure. As the seed passes the feed roll, it falls on to a guide-plate that carries it between the first and second rolls. After passing between these and being partially crushed, the seed falls on to a guide-plate on the other side, and is carried between the second and third rolls, where it is further crushed. It then falls on another guide-plate, which carries it between the third and fourth rolls, where it is ground still more. In large rolls it can be carried between a fourth and fifth roll before it receives the final crushing.





In the above illustration  
the kettle F, from which it p  
presses H. The cakes, after  
The parings are returned, to  
The presses H stand in





The crushed seed or meal is now raised by the elevator D (Fig. 10) into the kettle or heater F, where the mass is warmed by steam to the right temperature in order to facilitate the flow of oil when in the press, the heat also serving to coagulate albuminous matter in the grain. From the kettle the heated grain falls into the moulding machine or former G, where it is squeezed into cakes suitable for placing in the hydraulic press. The moulding machine also serves to accurately measure the amount of crushed or heated meal required for a cake, thus ensuring the production of cakes with little variation in weight.

The cakes thus formed are wrapped in cloth bags and placed in the hydraulic press (Fig. 8, and H, Fig. 10). One of the larger Anglo-American presses will take some sixteen cakes 28 in. by 12 in. each, separated from each other by a steel plate. When the press is full the pressure is slowly turned on, and the oil begins to flow from the compressed meal, at first slowly and then very rapidly, the oil running down the sides of the machine into a tank in which the presses stand, and from which it is forced by a pump to the filters or store tanks. When the pressure has been applied for three or four minutes the flow of oil practically ceases, the oil simply dripping from the compressed cakes until the pressure is released. If more presses than one are being used, they are filled one after the other until the whole battery of presses are charged. The meal cakes are allowed to remain under pressure from ten to forty minutes (the exact time varying with the special conditions) and then the pressure is released on the first press in the series and the ram allowed to descend. The cakes are removed one by one as the ram descends, and fresh charges of meal introduced wherever a cake is removed. The cakes as they are removed are placed on the paring machine, their cloth bags stripped off, and their oily edges cut away by the paring machine, these oily parings being reduced to meal again by small edge-stones J (Fig. 10), and returned to the kettle F (Fig. 10) to be worked up again. If a cage or circular box (clodding) press is employed the cake need not be pared—one great advantage of the latter system. The finished cakes are placed on racks in which they are allowed to stand until perfectly cool, when they are removed to the cake-house or store. The cake racks are usually placed in the most draughty part of the mill to assist the cooling process. Other similar small seeds are treated in much the same manner as linseed. Among these we may mention sunflower, mustard, China or Soya beans, some kinds of rape seed, poppy seed, and similar seeds requiring but a single pressing.

**Cotton Seed** also requires but a single pressing. Two varieties exist—the black seed and the white; the former has its husk quite clean and free from adherent cotton (example, Egyptian cotton seed), while the husk of the latter is covered with short white cotton fibres (examples, American cotton seed, Indian cotton seed). Both classes of seed are treated in England in much the same way as linseed, the only difference being that the seeds as they leave the rolls are ground beneath powerful edge-stones before passing on to the kettles. In the United States, however, the cotton seed is first decorticated, *i.e.*, the husk of the seed is entirely removed, only the resulting kernels or “meats” being pressed. The advantage of this treatment becomes obvious when it is realised that practically 50 per cent. of the seed is husk, and that consequently a mill removing this by using decorticators can treat twice as much seed as a mill of the same size, but without decorticators. The husks are used as cattle food, fuel, or manure, as the case may be.

**Castor Seed.**—This seed, being very rich in oil, is usually worked twice, the first time cold, and the second time hot. The seed must be very well cleaned before pressing, which operation is best carried out in cage presses, the seed being pressed in its natural state without any preliminary crushing at all. The best medical oil is the cold-drawn, and consequently it is greatly to the advantage of oil manufacturers to press out as much oil as possible at a single pressing. Immense presses have been erected for this purpose in some mills. A set of four giant presses is shown in the plate (Fig. 11), which represents a modern and improved type of press battery, designed by Rose, Downs, & Thompson, and used in some



large English oil mills. Each set comprises two presses, having cages or cake chambers 19 in. diameter and 9 ft. long internally. These chambers are finely perforated, so that while retaining the solid residue, they allow the oil and other fluids to escape. Each press has its own kettle, 60 in. by 26 in., while the rams are forced at a pressure of 3 tons on the square inch. The seed is fed whole to the kettles, are there heated by steam to about  $32^{\circ}\text{C}$ ., and afterwards pressed at 3 tons on the square inch. The resulting cakes contain from 8.5 to 10 per cent. of oil. The whole battery of four presses is worked by two men, and press a total weight of 2 tons of seed per hour.

Presses of this type are specially suitable for the first pressing of all kinds of very oily seeds, such as castor, sesame, ground nuts, copra, palm kernels, etc., producing a maximum quantity of first pressing oil, and reducing the oil in the cakes to such small proportions as to render a second pressing unnecessary, or permitting the remaining available oil to be extracted by solvents. In view of the high prices commanded by first-pressure oil, such presses effect a very great economy, although the first cost is high. In mills where less powerful presses are employed, the solid cakes resulting from the first pressing are ground up in suitable machinery, warmed, and pressed again.

A very effective modern process is to first press with a cage machine, and then extract the bulk of the oil from the resulting cake by solvents. Such extracted oil cannot be used for edible purposes, but is valuable for soap-making, lubricating, etc. The meal from the solvent contains only 1 per cent. of oil. This mixed process is largely worked on the Continent.

**Copra.**—This material is the flesh of the cocoa-nut. It is usually pressed twice owing to the difficulty of making cakes when pressed only once (unless very powerful presses are employed) and also on account of the very large amount of oil it contains. The copra is passed over a magnetic machine to remove all pieces of iron, smashed up in disintegrators, crushed in Anglo-American rolls, and automatically conveyed to the kettle or heater of the presses, which may be either "Anglo-American" or "cage" type, for the first pressing. Usually the material is worked cold the first time, the resulting cakes being ground up and heated for a final pressing. This process, with slight deviations, is used for treating all very oily seeds, such as ground nuts (*Arachides*), palm kernels, sesame, copra, etc.

#### (b) EXTRACTION OF OILS AND FATS BY MEANS OF VOLATILE SOLVENTS

The oil cakes obtained by the pressing process may contain anything between 7 and 10 per cent. of oil. Such cakes are often sold as a valuable cattle food. Occasionally, however, when larger quantities of oils and fats than can be obtained by pressing are desired, the rest of the oil is extracted by solvents, which can be easily made to remove all except, perhaps, 1 per cent. Bones are extracted in the same manner.

On the large scale three solvents are employed, viz., carbon disulphide, petroleum ether (benzine), and carbon tetrachloride.

**Chloroform** and **Ether**, although excellent solvents, are at present too dear to employ for extracting on the large scale. Trichlorethylene seems to be more stable than it used to be, and is said to produce a very high quality oil.

**Carbon disulphide**,  $\text{CS}_2$ , boils at  $46^{\circ}\text{C}$ . and has a sp. gr. of 1.293. It is a colourless liquid and smells something like chloroform. When impure, however, it contains evil-smelling sulphur compounds, from which it may be purified by distilling first over sodium carbonate and then over freshly pressed plant oils, which retain these impurities almost completely. Carbon disulphide easily inflames and so is a dangerous substance. Its vapour sometimes catches fire when in contact with hot metallic surfaces heated to about  $150^{\circ}\text{C}$ ., so that a violent explosion can be caused merely by a hot steam pipe or bearing heated by friction.

With **Petroleum ether**, boiling between  $80^{\circ}$ - $120^{\circ}\text{C}$ ., the danger of inflammation is much less and at the same time it is cheaper. It is, therefore, gradually replacing carbon disulphide. Carbon disulphide, however, is the better solvent, resinous fats and old palm oil being much more soluble in it than in petroleum.



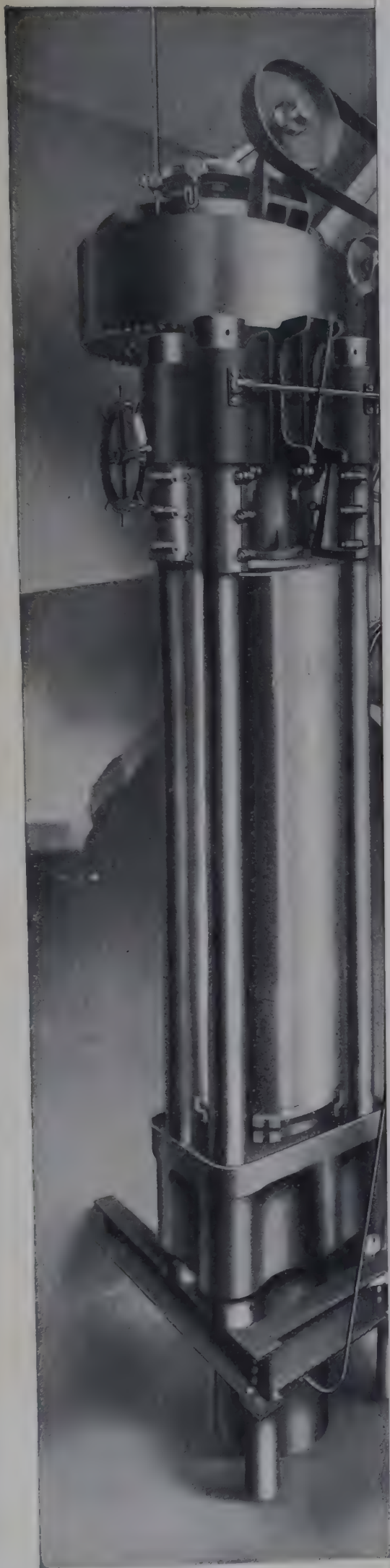


FIG. 11.—IMMENSE C





**Carbon tetrachloride**,  $\text{CCl}_4$ , is a good solvent, being easily volatile (B.P.  $76.5^\circ \text{C}$ ., sp. gr. 1.582) and non-inflammable. It is being employed for extracting bones and fats, the products obtained having a good colour; the odour of the tetrachloride can be completely expelled by blowing steam through the oil. Oils extracted by petroleum spirit always retain its smell. The main disadvantage that carbon tetrachloride suffers from is its great weight (sp. gr. 1.582), its dearness, and the fact that it attacks metal work. It must be noted that both carbon disulphide and carbon tetrachloride exert a poisonous physiological action, whereas petroleum spirit is not poisonous enough to affect the workmen.

Two methods of extraction are employed:—

1. Extraction by cold solvents.
2. Extraction by hot solvents.

**1. Cold Extraction.**—This is preferable as regards fire insurance and is largely practised with carbon disulphide for obtaining palm fats out of palm kernels.

The crushed and warmed seeds are charged into A (Fig. 12) (one of a battery of six closed iron cylinders) on to a perforated bottom F covered with sackcloth, and a stream of carbon disulphide from a reservoir is allowed to percolate through, passing in by B and flowing away by L (which is provided with a strainer) into the next cylinder of the series. The solvent thus flows through each cylinder in order, from the top to the bottom, remaining for a short time in each before passing on into the next. The solvent leaves the battery charged with about 50 per cent. of fat. The exhausted cylinders are heated by a current of steam passed in through C, and the solvent still in the seeds is driven off through D, condensed in long tubes, and used again. The solvent containing the fats is pumped to the steam-heated still R, where the solvent is boiled off by the steam coils J K (Fig. 13). The vapours rise through M and the solvent is recovered by condensing the former in a special condenser. The residue of oil or fat left in R is freed from solvent by blowing steam through it, after which the oil is run off through P and allowed to stand until the condensed water has separated out. The battery of vessels is so constructed that any one can be made the last of the series ready to be discharged and refilled with fresh meal, so that the process is a practically continuous one, the only time lost being in the actual refilling and discharging, which is effected by removing the clamped-down cover from A.

The loss of solvent amounts to only 0.5 per cent. to 1 per cent. on 100 parts of fat. The fat is digested with a little concentrated sulphuric acid, and drawn off into wooden vessels. Fat obtained from carbon disulphide extraction is nearly odourless, whereas that obtained by this process from benzene still retains a slight odour of this solvent and may be used for making soap.

**2. Hot Extraction.**—In this process the extraction takes place continuously with a limited amount of solvent charged once for all into the apparatus, which is merely an enlarged form of the Soxhlet extractor employed in the laboratory.

An apparatus extensively used for extracting fat from bones by means of benzene is illustrated below.

The degreasing boilers A, A (Fig. 14) are filled with air-dried bones which rest on the perforated floor *nn*. The lower space B is heated by means of a steam coil *d*. By

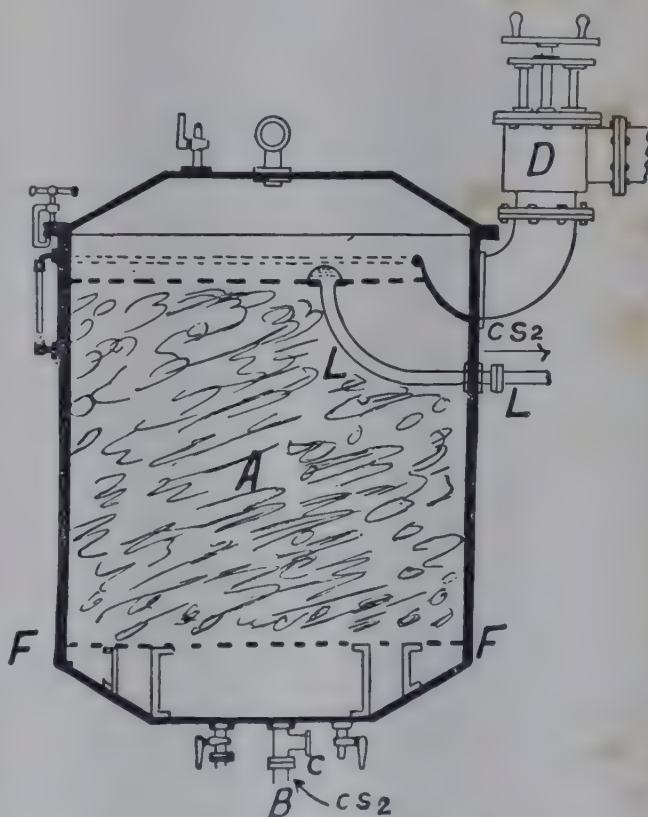


FIG. 12.—Cold Extraction Plant.



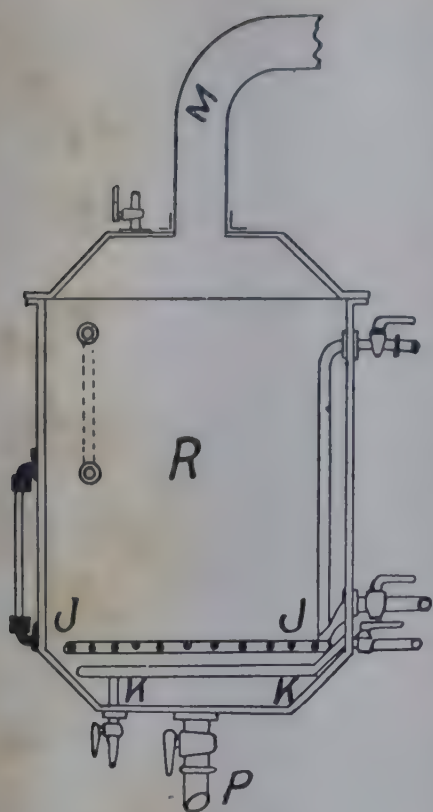


FIG. 13.—Still for Cold Extraction Plant.

away by *w*. From the reservoir *g* the benzine flows into the lower-situated vessel *c* and is used over again.

It will be seen that very little benzine is necessary to effect extraction, the same benzine being used over and over again. Bones treated thus yield 6-7 per cent. of fat. A typical modern extraction plant for scents is described on p. 134.

means of a nozzle *b* live steam can be blown in. Benzine is heated in the boiler *c* by means of a steam coil, and the benzine vapour, rising upwards, is superheated to  $120^{\circ}$ - $130^{\circ}$  C. in the tubular superheater *d* by means of high-pressure steam. The superheated benzine vapour issues from small holes in the tube *r* and streams upwards through the bones. Part of the vapour condenses here, and flows down, carrying with it fat extracted from the bones, and collects in *B*, where it is continually boiled by means of the steam coil *d*. Part of the benzine vapour escapes in the gaseous state through *p*, and, together with the water simultaneously expelled from the bones, is condensed in the cooler *E*. The superheating of the benzine vapour is necessary in order to dry the bones and thus enable the solvent to more thoroughly penetrate them. When no more water passes over the process is complete. A current of live steam is then blown through the apparatus by means of the nozzle *b*, and this soon drives the benzine out of the fat in *B* as well as that still remaining in the bones in *A*. The benzine thus expelled, together with condensed steam, collects in the water-separator *F*. The benzine being lighter than the water, collects on the surface and flows continually out at *g* into the benzine reservoir *G*, the water flowing

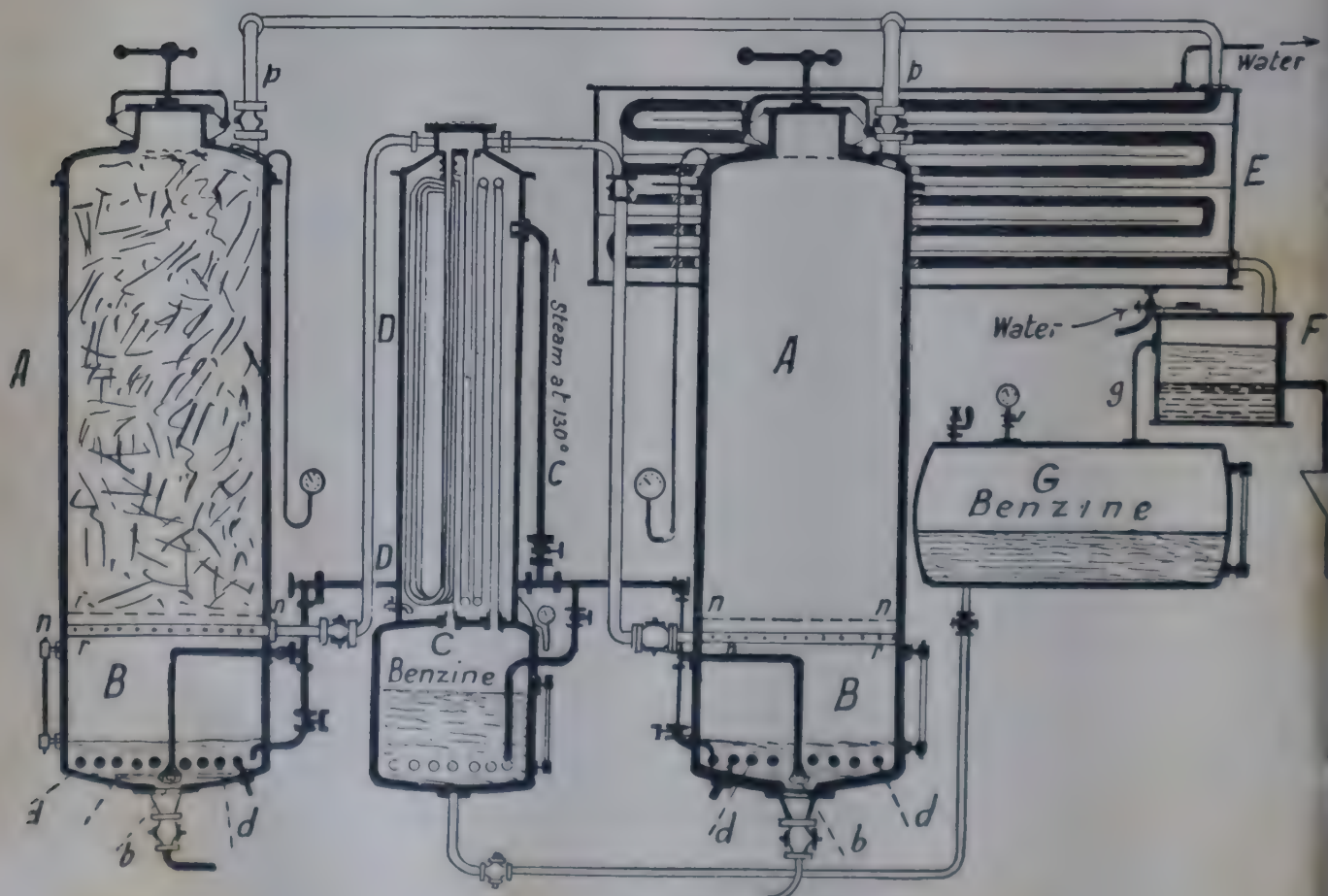


FIG. 14.—Hot Extracting Plant.



## Merits and Demerits of the Methods of Extracting Oils and Fats by Pressure and by Solvents

1. Edible oils and fats cannot at present be prepared by extraction by solvents, since enough solvent is always retained to impart a nauseous taste. Such oils and fats are, therefore, only used for soap-making and other technical purposes.

2. Extracted meal by itself is not suitable for feeding cattle. On the Continent it is mixed with press cake and sold for this purpose. Press cake is, however, far better as a food material from a stock-raising point of view than the cakes obtained by the extractive process, even when these latter have oil or fat added to them so as to equal the proportion contained in the pressed cakes.

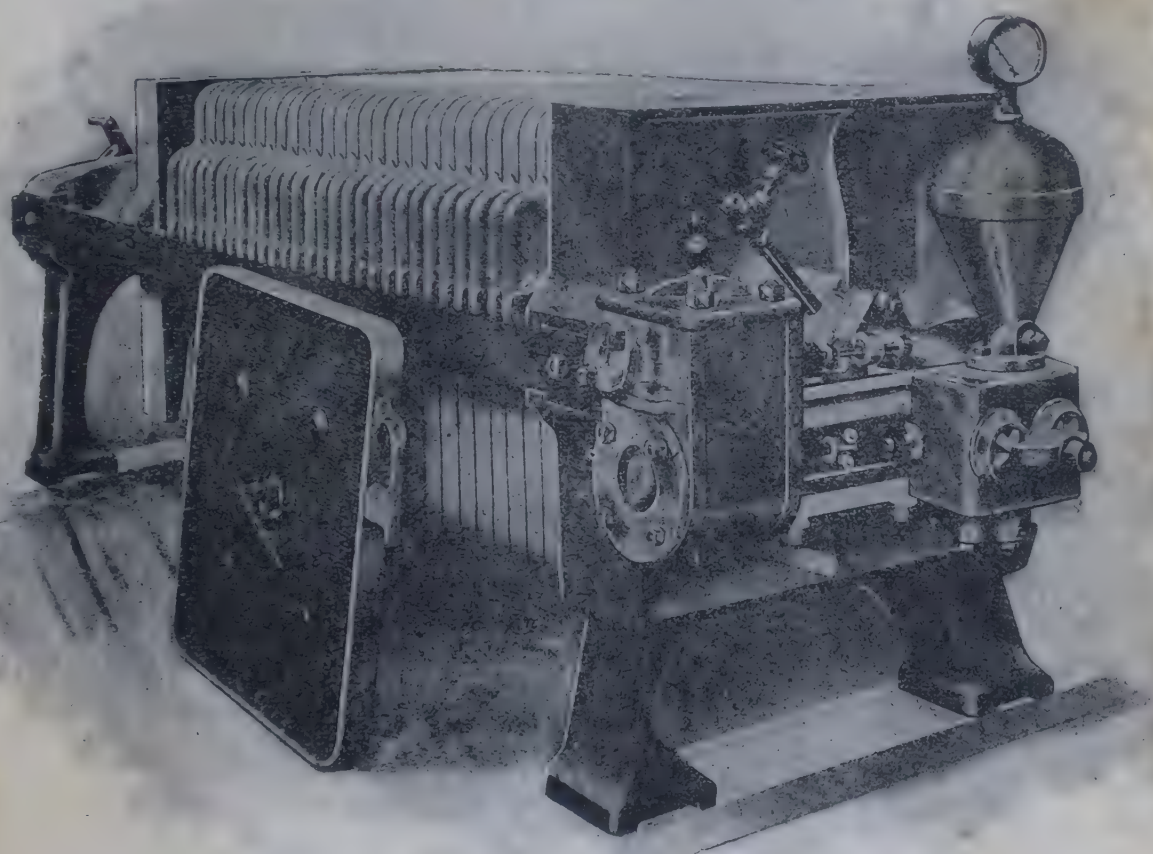


FIG. 15.—Hydraulic Oil Filter Press, with self-contained Steam Pump.  
(Rose, Downs, & Thompson, Hull.)

3. The solvent process extracts the fats and oils to a far larger extent than the pressure process, only about 1 per cent. of oil being left in the extracted seed, against 7-10 per cent. in the pressed. In many cases a combination of pressure and solvent processes is the best, oil being first expressed and sold as edible oil, and the residue, still fairly rich in oil, is extracted, and the oil thus obtained sold for soap-making and other technical purposes.

## General Methods of Refining and Bleaching Oils and Fats

The actual process adopted depends somewhat upon the nature of the oils. If these are fresh and well made, they may be worked up directly into technical products without any refining.

(a) **Tanking and Filtering.**—The oils are run into tanks and allowed to stand. Dirt and impurities settle to the bottom, and the supernatant oil becomes clear. Sometimes oils are tanked for months or years at a time (*e.g.*, linseed oil).

A much quicker process is direct filtration, which avoids the loss of time and storage space necessitated by the old plan of subsidence, the sole product of the oil mill being a cake and bright oil, the residue in the filter being worked back again in the mill. The filtration is effected by pumping the oil direct from the hydraulic presses through a filter press (Fig. 15). This consists of a series of grooved iron plates, hollow on the inside, which are clamped tightly together, and which contain cloth separating them. The oil is thus forced through a succession of cloth filters, and the solid matters are caught and deposited in the spaces between the cloths.

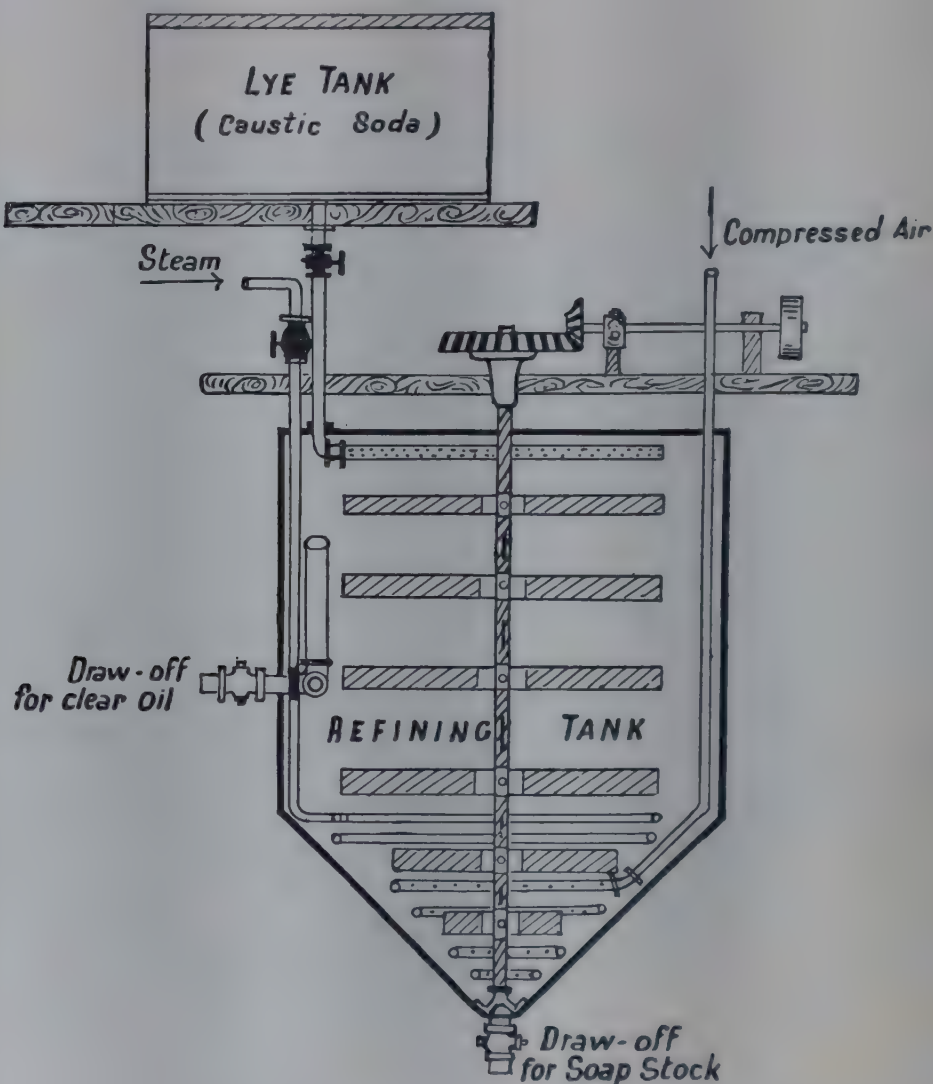


FIG. 16.—Cotton-Seed Oil Refining Tank.

Nothing but oil comes in contact with the plates, the oil passing out at the end pure and bright.

(b) **Treatment with Caustic Soda or Sulphuric Acid.**—The oil is washed in special tanks with a solution of caustic soda or sulphuric acid. Thus *cotton-seed oil* is pumped into a large tank of the construction shown, then heated by steam to  $30^{\circ}\text{C.}$ , and the proper amount (which depends upon the quality of the oil) of caustic soda solution ( $74^{\circ}\text{Be.}$ ) run in and mixed thoroughly either by mechanical agitators, or by a current of air blown through the liquids for fifteen minutes. On standing, a sediment of coagulated albuminous and mucilaginous matter from the oil settles at the bottom of the tank together with the excess of caustic soda solution. The oil is cooled and siphoned off from the sediment to



a finishing kettle, where it is washed free from caustic soda by a stream of water. The wash water is withdrawn from the bottom of the kettle until oil comes; then fresh water is added, and the process repeated until the oil is free from alkali. During this operation a blast of air is blown through the liquids, or mechanical agitators are used, in order to thoroughly mix the oil and water.

Finally moisture is expelled by heating the oil gently by steam pipes to a temperature not higher than 50° C., while a current of air is blown through. The last traces of moisture are sometimes removed by adding plaster of Paris and filtering. Filtration through a layer of common salt also removes all moisture.

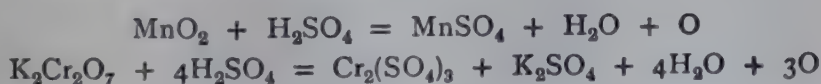
Many industrial oils are purified as above, but with a solution of *sulphuric acid*. About 2 per cent. of sulphuric acid of 66° Be. mixed with an equal volume of water, is run into the oil contained in a lead-lined tank; then the liquid is agitated by an air blast, warmed for about one hour, settled, the acid run off at the bottom, and the oil washed with water and caustic soda until free from acid; finally the clear supernatant oil is decanted and filtered.

Edible oils and oils for lubricating purposes are nearly always purified with caustic soda, which removes the nauseous tasting free fatty acids. A trace of mineral acid spoils the oil for lubricating purposes.

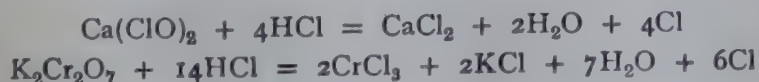
**Deodorisation of Edible Fats.**—Certain high-grade edible fats and oils are sometimes extracted with alcohol. They are stated to be rendered perfectly odourless and tasteless by this process, and so can be employed in the manufacture of high-class margarine and similar comestible fatty products.

Two methods are well known for the deodorisation of cocoanut oil:—(1) **Washing out the odoriferous bodies with alcohol.** This removes the fatty acids, and also such substances as phytosterol. *Chevreul* and *Schlinck* employ a joint process of washing with alcohol followed by treatment with charcoal. For a recent patent see *Urbain* and *Friégé* (French Patent, 361,966, 1905). (2) **Volatilisation by steaming.** *Jeserich* and *Meinert* (1882) passed high-pressure steam at 6-8 atmospheres into the fluid oil for two to three hours; the non-volatile fatty acids left were then removed by adding 0.25 per cent. of calcined magnesia, and the magnesium soap formed is then skimmed off the surface. *Klimont* (English Patent, 3,164, 1902) neutralises the oil with alkali before treating with steam.

(c) **Bleaching with Chemicals.**—Actual bleaching with chemicals is only resorted to in the case of inferior or very dark oils and fats. Bleaching by means of oxygen in a nascent state is usually effected by adding manganese dioxide or potassium bichromate and sulphuric acid:—



Sometimes bleaching powder or potassium bichromate, together with hydrochloric acid, is used, when chlorine is evolved, thus:—



No general rule can be given as to the best process to employ in a given case; thus *tallow* is usually bleached with manganese dioxide and sulphuric acid, while *palm oil* with bichromate and hydrochloric acid. The quantity of chemicals employed must be as small as possible, the time of interaction as short as possible, and the temperature as low as is compatible with efficiency. The glycerides may be seriously damaged if such conditions are not rigorously observed.

It will be sufficient if we describe the Sulphuric Acid Bichromate Oxidation Process. The melted oil or fat at a temperature of about 38° C. is pumped into a lead-lined chemical treatment tank, compressed air is blown through it in order to thoroughly mix the contents, while the requisite amount of bichromate solution (1 bichromate : 4 water by weight) is run in. The mixing is continued for about one hour while the contents of the tank are simultaneously warmed by a steam coil. Finally the liquid is allowed to settle, the acid run off at the bottom, and the oil washed with water to remove acid.



**Palm Oil** is now bleached on quite a large scale by means of oxygen, and more recently, by ozone. An apparatus for bleaching palm oil by atmospheric oxygen is represented in Fig. 17. A closed vessel is fitted at A with a steam jet exhauster, and a copper heating coil K K. At the bottom of the vessel is an annular air-distributing pipe with a large number of small holes connected to an inlet pipe carrying compressed air, oxygen, or ozonised oxygen.

The palm oil, which has been previously liquefied, and allowed to stand so that the water and dirt may settle to the bottom, is run into the iron vessel, heated by the steam coil to  $100^{\circ}\text{C}$ ., and air is blown through. The oxygen removes most of the colouring matter, and as in this process no strong chemicals are used, the natural properties of the oil are not affected. The process may take two hours. Rank fish oils are deodorised and decolourised by this process. Sometimes instead

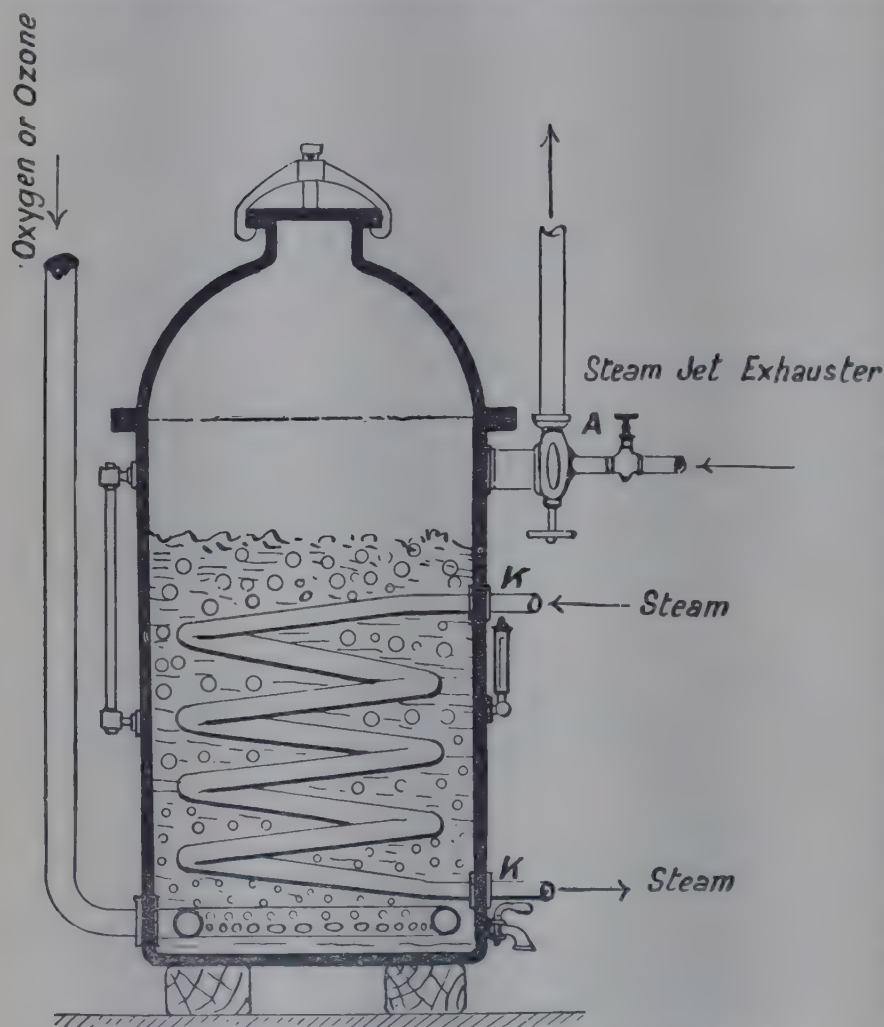


FIG. 17.—Plant for Bleaching and Deodorising Palm Oil by means of Oxygen or Ozone.

of air steam at a temperature of  $110^{\circ}\text{C}$ . is driven through the oil, ten hours' steaming being sufficient to deodorise 4 tons of oil. Another method of bleaching palm oil (and which yields good results with almost all other kinds of oils) is this: Melt, say, 100 parts of palm oil in a boiler, and when liquid add a solution of chloride of lime, made by dissolving 7 parts by weight of the chloride in water for every 84 parts by weight of oil; mix intimately, cool, and cut the hardened mass into small pieces, and leave exposed to the air for a few weeks. Next place the fat in a boiler lined with lead, add a 5 per cent. solution of sulphuric acid, equivalent in total amount to the lime chloride, heat, separate the oil from the acid, wash, and allow to solidify.

**Bone Fat** is often bleached as follows: place the fat (which must be free from gelatine and calcium phosphate) in an iron pan, add an equal weight of brine of  $14^{\circ}$ - $15^{\circ}\text{Be}$ ., boil for three hours, allow to stand twelve hours, draw off the fat into a wooden vessel, and treat with a mixture of 2 parts potassium bichromate dissolved in boiling water, and 8 parts of hydrochloric acid ( $22^{\circ}\text{Be}$ ). This quantity is sufficient for 400 parts of fat. Leave the mass standing, stirring at intervals, when decoloration proceeds gradually. When complete, wash the fat with hot water.

**Linseed Oil** may be refined by placing 236 gallons into a copper boiler, adding 6 lbs. of oil of vitriol, and stirring together for three hours. Next add 6 lbs. of fuller's earth mixed with 14 lbs. of hot lime, stir three hours, run off the oil into a copper vessel containing an equal volume of water, boil three hours, draw the fire, and when the oil is cold, run off the water and let the mixture settle for some weeks.



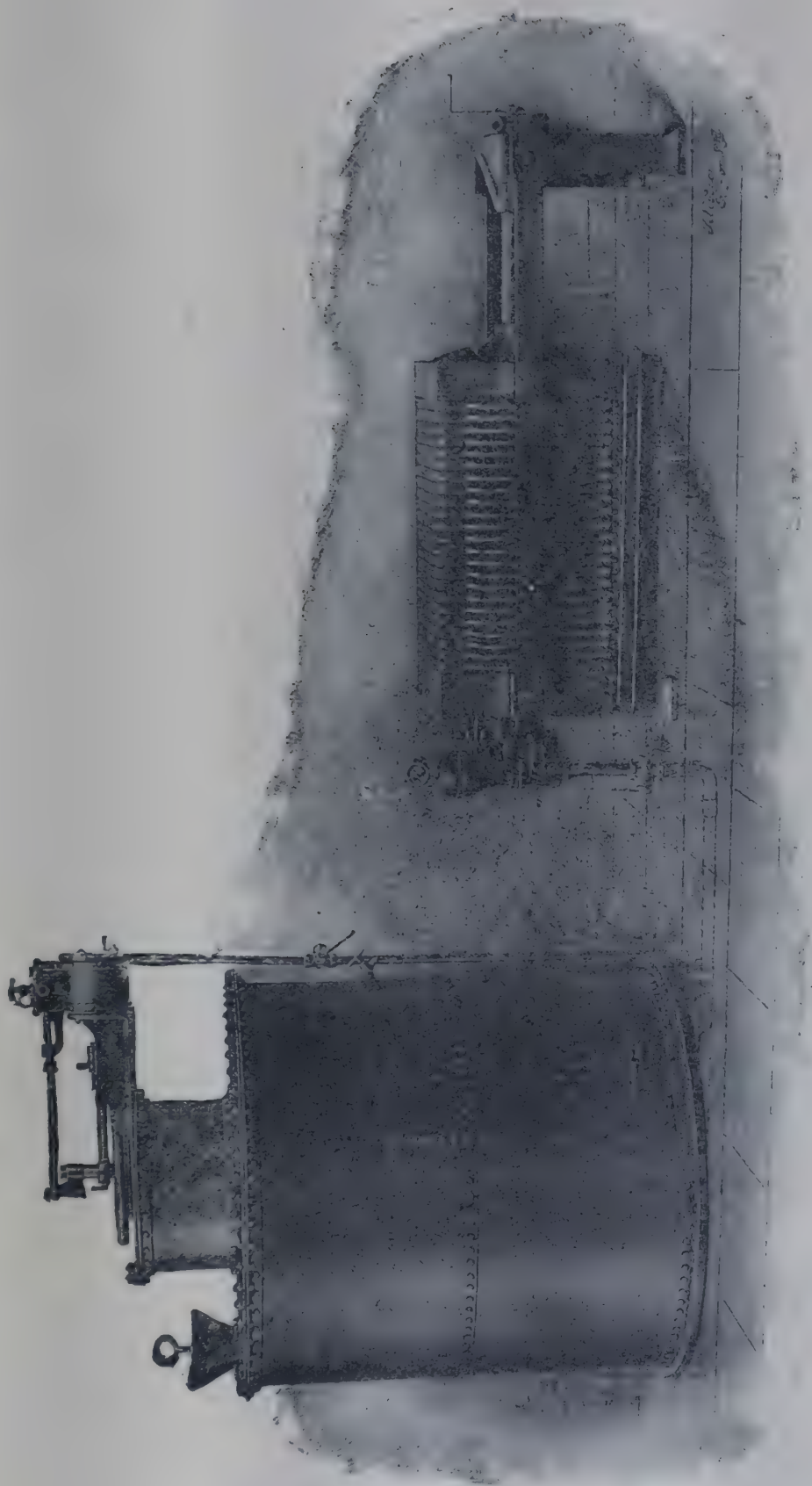


FIG. 18.—Fuller's Earth Plant. For treating lard, cotton-seed oil, cocoanut oil, ground-nut oil, etc.  
(Rose, Downs, & Thompson, Hull.)

It is frequently decolourised by a 30 per cent. solution of  $\text{FeSO}_4$  or with  $\text{KOH}$  followed by  $\text{K}_2\text{Cr}_2\text{O}_7$  and  $\text{HCl}$ . Other ways used are:—

1. *Sun Bleaching*, employed for the most expensive varieties of artists' oil. The oil is exposed to sunlight in shallow trays under glass.

2. *By Hydrogen Peroxide*.—Shake the oil in a glass bottle with a 5 per cent. solution of hydrogen peroxide, and allow to stand for some days, shaking occasionally. The oil clarifies and is poured off from the water at the bottom.

3. *By Potassium Permanganate* (suitable also for poppy oil).—Place 25,000 parts of oil in a large glass balloon, add a solution of 50 parts of potassium permanganate in 1,250 of water, stir well, allow to stand twenty-four hours at a gentle warmth, then add 75 parts by weight of powdered sodium sulphite, agitate well, add 100 parts of hydrochloric acid, again agitate, and allow to stand until decolourisation takes place. Wash the oil with water rendered milky with chalk powder until free from acid, and finally separate the water, and filter off the oil through anhydrous sodium sulphate.

Bleaching of linseed oil with chloride of lime and hydrochloric acid, or calcium bichromate and sulphuric acid, is sometimes employed, but the operation requires great care and is sometimes dangerous.

**Decolourisation with Fuller's Earth, Animal Charcoal, etc.**—Animal charcoal is by far the best decolourising (and deodorising) agent known, yet on account of its cost it can only be employed for edible oils and fats. More usually fuller's earth or powdered kaolin is used, being less expensive than charcoal. The oil is treated with the decolourising powder in a special mixer. The apparatus shown in Fig. 18, p. 37, is that manufactured by Rose, Downs, & Thompson at Hull. It consists of a steam-jacketed cylindrical steel tank with a contracted neck at the top, and provided with a powerful stirring apparatus for rapidly mixing the fuller's earth with the oil. The tank is filled to the underneath part of the neck with the oil or fat to be treated (which has been previously heated to  $40^\circ$ - $60^\circ$  C.), and 3.5 per cent. of fuller's earth (the exact quantity depending upon the amount of colour to be removed) rapidly stirred in. The earth should be in the form of a perfectly dry powder. It is a silicate of aluminium.

Oils and lard, which are to be used as food, must not be left in contact with the fuller's earth for more than fifteen minutes after mixing or they begin to acquire an earthy flavour. Consequently the materials must be separated as rapidly as possible after they have been stirred round for the right time.

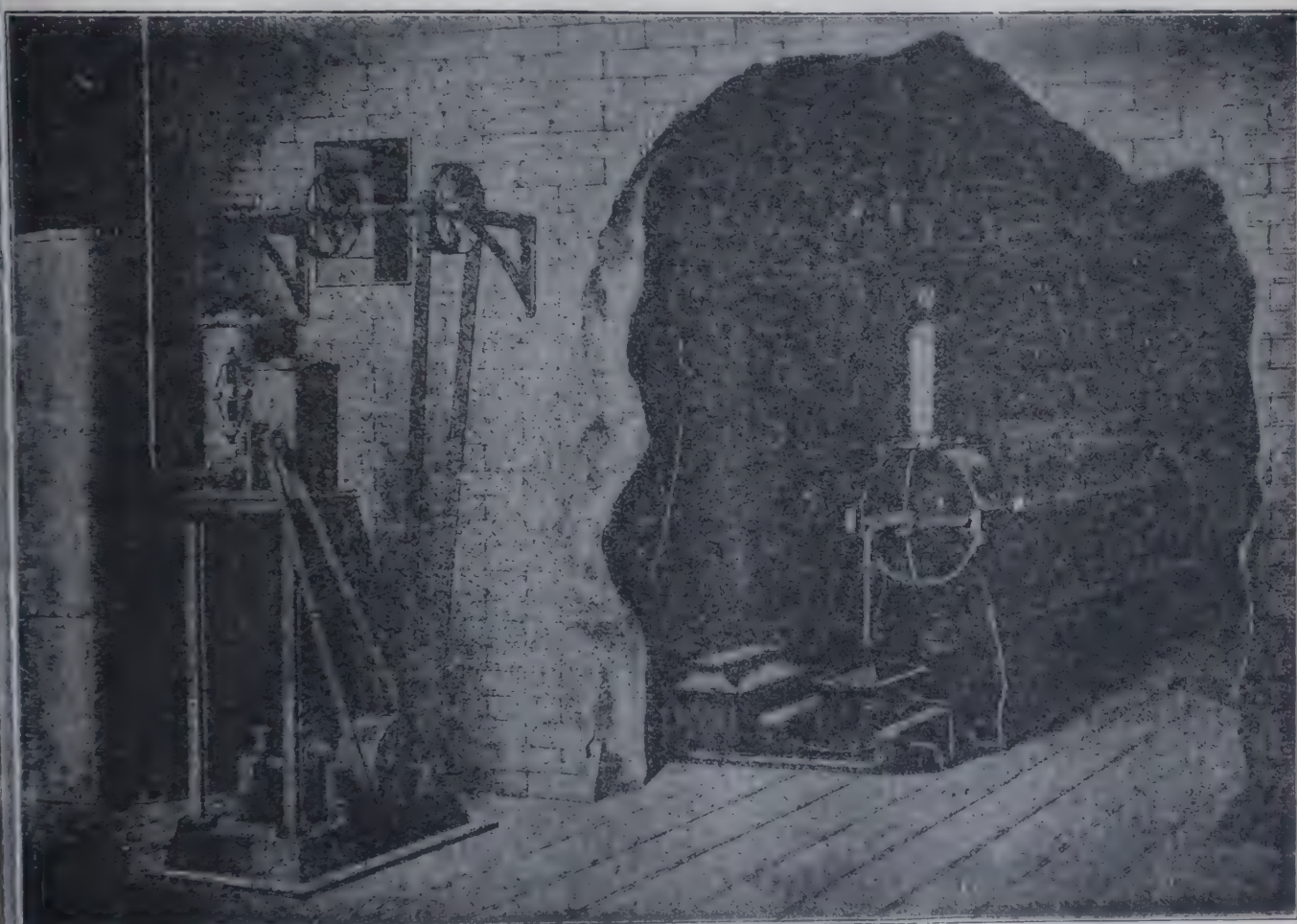
The oil or lard is rapidly pumped away through the filter press, which retains the fuller's earth, the oil passing on through the filter cloths. Finally steam is blown through the press so as to free the cakes from oil. When the press is opened the earth falls out as a powder upon the floor, little or no oil being left in it. When dealing with fats or waxes which are solid at ordinary temperatures (e.g., tallow, lard, paraffin wax) the filters are steam-jacketed so that their contents can be maintained at any temperature necessary to prevent the solidification of the fat in the presses.

**Demargination of Oils.**—Many of the vegetable oils (such as cotton-seed, arachis, fish, and some sorts of olive oil) deposit a crystalline mass of "stearin" on standing. It is very important that edible oils should not solidify at temperatures near the freezing point. Also lubricating oils must necessarily remain liquid at low temperatures, an oil still fluid at  $-15^\circ$  C. being demanded for railways in the United States. Such oils are known as "Winter Oils."

Hence many natural oils must be "demarginated" before they can be placed on the market. Originally the process consisted in simply storing the oil in large vessels through the winter, when the "stearine" separated out as a white solid mass at the bottom. The supernatant oil, when drawn off, formed the "winter oil." This process is still used for arachis oil, but in other cases the cooling is artificially carried out, and the stearine removed by forcing the oil through a filter press.



Fig. 19 shows an oil-cooling and filtering plant designed by Rose, Downs, & Thompson, of Hull. The oil is placed in the tank c, which is provided with agitators and a cooling coil. The cooling effect is produced by allowing anhydrous ammonia, condensed to a liquid by the pump B, to expand through the cooling coil in the tank c. Here the liquid suddenly expands into a gas, producing intense cold in so doing. The oil, under the influence of this cold, and aided by a vigorous mechanical stirring, deposits its stearine in the solid form at the bottom of the tank. The ammonia, now issuing as a gas from the cooling coil, is recondensed to a liquid by the pump B, the compression being carried out in the tank c, filled with cold water, which effectively carries away the heat generated in the operation. The process is continued until the oil is reduced to the temperature at which it is desired to remove the stearine. When this point is reached the oil is drawn off and pumped through the filter press D, which removes any suspended stearine crystals.



A

B

C

D

FIG. 19.—Oil-Cooling and Filtering Plant, for the separation of stearin and olein.  
(Rose, Downs, & Thompson, of Hull, England.)

Oil which has been treated in this way will always remain clear and bright at any temperature above that at which the stearine has been removed.

The separated stearine is a valuable product, being largely used for making margarine, margarine cheese, lard substitute, etc. etc.

## VARIETIES OF FATS, FATTY OILS, AND WAXES

### Classification

For convenient description we divide the oils and fats under the headings:

- 1) Animal fats and oils, (2) Vegetable fats and oils, (3) Waxes.



**1. Animal Fats and Oils.** These include **Fish Oils**.—The oils derived from marine animals are characterised by their odours and, analytically, by a high Maumené and iodine value.

**2. Vegetable Fats and Oils** may be conveniently arranged, according to their iodine values, into (a) **Solid fats**, (b) **Non-drying oils**, (c) **Semi-drying oils**, (d) **Drying oils**.

No rigid line can be drawn between these classes, as they merge into each other. The iodine value affords a means of ascertaining roughly their constitution and gives a rough basis of classification. Triolein has an iodine value of 86.2 and consequently if an oil absorbs more than 86.2 per cent. of iodine it probably contains the glyceride of an acid of the linolic or linolenic series. Now linolic and linolenic acids and their glycerides readily absorb oxygen from the air—a property not possessed by oleic acid and triolein—and it is due to the presence of **trilinolin** and **trilinolenin** that the drying oils owe their property of drying by absorbing of oxygen on exposure to air. Since the iodine value of pure trilinolin is 173.6, oils having an iodine value of above 170 may be classified as **drying oils**; those having an **iodine value** of 90 or lower may be called **non-drying oils**; while oils having intermediate iodine values may be called **semi-drying**. In practice it is found that **oils** with iodine values above **140** have valuable drying properties; those with iodine values 100-140 are semi-drying, since they are able to absorb a certain quantity of oxygen, but will not dry completely when exposed to the air in a thin layer. Oils with iodine values less than 100 are practically without drying value.

The **Fish oils** form an exception to this rule; some of them have iodine values as high as that of linseed oil and absorb large quantities of oxygen; yet they do not usually dry to a hard layer. Their unsaturated acids are of a different constitution from linolic and linolenic acids.

**3. The Solid Waxes of Animal and Vegetable Origin**, and the liquid waxes (sperm oil, bottlenose oil) are characterised by their high content of higher alcohols (unsaponifiable matter). They do not contain glycerol. They are therefore treated as a separate class under the title of **Waxes** (see p. 52).

### Varieties of Animal Fats and Fatty Oils

**Tallow**, the solid fat of oxen and sheep, consists of tristearin, tripalmitin, and 40-46 per cent. triolein.\* Mutton tallow melts 45°-55°; oxen tallow 45°-50° C.; solid point, 40°-47°; Reichert value, 0.25; Hehner value, 96; iodine value, 35-46; saponification value, 193-198; sp. gr. 0.86 at 100°, 0.94-0.95 at 15°. Melting point of fatty acids, 38°-49° C.; solid point, 38°-48°.

**Tallow Oil**.—Very similar constants to lard oil; iod. val. = 32-57; Maumené, 41°-44° C.

**Lard** is the rendered fat of pigs. American lard often contains cotton-seed oil and tallow.—M.P. 30°-49°; sol. pt. 23°-30°; sap. val. 195-197; iod. val. 50-77; Hehner val. 95-98; sp. gr. (100° C.) 0.860-0.864. The separated fatty acids have sol. pt. 34°-42°; mol. wt. 278; iod. val. 64; refract. index, 1.439 (60° C.).

**Lard Oil, Oleo Oil**.—Acid val. 0.4; sap. val. 193; Hehner val. 97.4; Reichert-Meissl val. 0.4-0.9; iod. val. 53-88. Insol. fatty acids have sap. val. = 206.

**Goose Fat**.—M.P. 25°-34°; sol. pt. 18°-20°; sap. val. 184-198; iod. val. 60-72; Reichert-Meissl val. 0.2-0.3; Hehner val. 92-96; sp. gr. 0.91-0.93.

**Butter Fat** is described under Butter.

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\* Recent researches have shown the presence of mixed glycerides.



**Bone Fat**, from fresh bones.—M.P.  $21^{\circ}$ - $22^{\circ}$ ; sol. pt.  $15^{\circ}$ - $17^{\circ}$  C.; sap. val. 190-195; iod. val. 46-56; sp. gr. 0.914-0.916 at  $15^{\circ}$  C. **Mixed fatty acids**, M.P.  $30^{\circ}$ ; sol. pt.  $28^{\circ}$ ; neut. val. 200; iod. val. 56-58. Fat extracted from old bones by benzine is dark, smells unpleasantly, contains calcium soap (derived from mineral matter of bones) and free fatty acids. Used for soap-making.

**Sheep's Foot Oil, Horse Foot Oil, and Neat's Foot Oil** are yellowish oils valuable for lubricating (since they do not easily become rancid), obtained by boiling the feet of cattle with water.—Sp. gr. 0.91-0.92 at  $15^{\circ}$  C.; sap. val. 194-197; iod. val. 73-75; Maumené test,  $38^{\circ}$ - $50^{\circ}$  C. **Mixed fatty acids**, sol. pt.  $20^{\circ}$ - $26^{\circ}$  C.; iod. val. 66-76; neut. val. 200-206.

**Horse Fat**, yellowish, often becomes rancid.—Sp. gr. 0.89-0.93 at  $15^{\circ}$  C., 0.79-80 at  $100^{\circ}$  C.; M.P.  $40^{\circ}$ - $50^{\circ}$ ; sol. pt.  $22^{\circ}$ - $48^{\circ}$ ; iod. val. 75-85; Reichert val. 0.33; Hehner val. 95. **Mixed fatty acids**, M.P.  $36^{\circ}$ - $41^{\circ}$ ; sol. pt.  $30^{\circ}$ - $33^{\circ}$ ; iod. val. 74-84.

**Fish Oils** are usually fluid, containing glycerides of oleic, stearic, physetolic acids, and other unsaturated acids. Unless of the best medicinal qualities these oils are dark, evil-smelling fluids in consequence of small quantities of decomposition products of decaying fish (trimethylamine).—Sp. gr. 0.92-0.933; sap. val. 170-200; iod. val. 100-110; Reichert val. 1.5-2.2; Hehner val. 95; Maumené's test,  $100^{\circ}$ - $128^{\circ}$  C. **Mixed fatty acids**, sol. pt.  $21^{\circ}$ - $28^{\circ}$ .

Fish oils are now used both in the ordinary and the enamel leather trade with excellent results; and the enamel leather produced, whilst not quite so glossy as when linseed oil is used, is said to be more flexible and less liable to crack; also for soap-making, and in the manufacture of printing ink.

When cooled, fish oils often deposit solid masses of **Fish Stearine** (fish tallow).

**Sod Oil (Dégras)** is the waste oil obtained in the process of chamoising leather. The leather is soaked in fish oils and then exposed to the air. Oxidative and fermentative processes set in which convert the contained oil into sod oil. The oil is extracted from the leather by means of sodium carbonate solution, and then separated from the emulsion it thus forms by the addition of dilute sulphuric acid. A similar product is obtained by blowing air through fish oils heated to  $120^{\circ}$  C. Sod oil consists principally of unchanged fish oil, owing its valuable properties to the presence of a resinous acid "dégras former," of unknown constitution, soluble in alkalis, insoluble in petroleum ether; it is this substance which makes sod oil so suitable for oiling dressed leather.—Sp. gr. 0.92-0.98 at  $15^{\circ}$  C.; refract. index, 1.475-1.478; acid val. 8-28; sap. val. 180-190 (from shark-liver oil only, 143); acetyl val. 22-48; iod. val. 70-100.

## Varieties of Vegetable Fats and Oils

### (a) SOLID VEGETABLE FATS (*i.e.*, M.P. above $20^{\circ}$ C.)

**Cacao Butter** is expressed from cacao beans in the process of working them into cacao.—M.P.  $30^{\circ}$ - $34^{\circ}$ ; sap. val. 192-200; iod. val. 34-37; Reichert-Meissl val. 0.83; refract. index ( $60^{\circ}$  C.), 1.45. Sp. gr. 0.96-0.97 at  $15^{\circ}$ , 0.85-0.86 at  $100^{\circ}$ . The insol. acids have M.P.  $48^{\circ}$ - $53^{\circ}$ ; neut. val. 190; iod. val. 32-39; refract. index, 1.42 ( $60^{\circ}$  C.).

**Chocolate Fats**.—The best substitutes for cacao butter are made by expressing, at a temperature slightly over the normal atmospheric temperature, the solid fats which crystallise out from palm-nut and cocoa-nut oils. Small quantities of animal fats are sometimes added to raise their melting points; these, however, sometimes impart an unpleasant taste, and it is better to use for the purpose vegetable fats such as those from margosa or mowra oil. Sap. val. 242-254; iod. val. 6-10; M.P.  $25^{\circ}$ - $30^{\circ}$ ; Reichert-Meissl, 3.5-8.0.



**Nutmeg Butter** is obtained from the seeds of *Myristica officinalis*.—Sp. gr. 0.94-99 at 15°, 0.88-90 at 100°; M.P. 38°-50° C.; acid val., 22; sap. val. 156; iod. val. 40-80.

**Chinese Vegetable Tallow** is the hard fat which coats the seeds of the Chinese tallow tree.—M.P. 44°-53° C.; sap. val. 200; iod. val. 32.

**Japan Tallow** is a similar fat which surrounds the berries of certain sumach trees which flourish in China and Japan; rich in palmitin.—M.P. 50°-53°; sap. val. 220; iod. val. 4-15.

**Palm Oil**, obtained in very large quantities from the fleshy parts of the fruit of certain palm trees, is a fat having a sweetish taste and an odour resembling that of violets, which persists even after bleaching with air at high temperatures, and after making into soap. It consists principally of tripalmitin, triolein, and free fatty acids; the proportion of the latter is sometimes very large in commercial specimens owing to a process of enzyme hydrolysis which goes on in the shipped oil.—Sp. gr. 0.92 at 15° C., 0.85 at 100° C.; sol. pt. 31°-38°; M.P. 27°-42° C.; sap. val. 202; iod. val. 51-57; Reichert-Meissl val. 0.9; Hehner val. 95; refract. index (60° C.) 1.451. Insol. fatty acids have sol. pt. 36°-45°; M.P. 47°-50°; neut. val. 204-206; iod. val. 53.

**Palm-kernel Oil**, **Palm-nut Oil** is obtained from the kernels of the palm tree fruit, and contains much lauric acid. It is easily saponified by cold concentrated caustic soda solution.—Sp. gr. 0.91 at 40°, 0.87 at 100° C.; sol. pt. 23° C.; M.P. 23°-30° C.; sap. val. 250; iod. val. 10-17; Reichert-Meissl val. 5-7; Hehner val. 91; refract. index (60° C.) 1.4431. Insol. fatty acids have sol. pt. 20°-25°; neut. val. 251-265; iod. val. 12.

**Cocoa-nut Oil** is the fat obtained from the kernels of the cocoa-nut. The fleshy part of the kernel, called copra, contains a large amount of fat, which consists of glycerides of lauric, myristic, palmitic, and other acids, some of them volatile. The fat, like palm-kernel oil, is easily saponifiable in the cold by concentrated caustic soda solution. Largely used for soap and margarine manufacture. For the latter purpose it is deodorised (1) by washing with alcohol, or (2) by treating with superheated steam (see p. 35).—Sp. gr. 0.92 at 15°, 0.86-0.90 at 100° C.; sol. pt. 16°-23° C.; M.P. 23°-26°; sap. val. 250-260; iod. val. 8-9; Reichert-Meissl val. 7-8; refract. index, 1.43 (60° C.). The fatty acids have sol. pt. 20°-25°; neut. val. 258; iod. val. 8-9.

**Mahwa Butter**, **Mohwrah Butter**, **Mohrah Seed Oil** (from *Bassia latifolia*).—M.P. 23°-26°; acid val. 5-11; sap. val. 187-194; Hehner val. 95; Reichert-Meissl val. 0.4-1.0; iod. val. 50-68. Insol. fatty acids, sap. val. 200.

**Mowrah Seed Oil** (from *Bassia longifolia*).—Sap. val. 196-202; iod. val. 50.

**Myrtle Wax**.—Acid val. 3; sap. val. 205-212; iod. val. 1.9-4. **Fatty acids** have neut. val. 230.

**Shea Butter**, **Bambuk Butter**, **Karité Oil**, from the seeds of *Bassia Parkii* (West Africa and Soudan).—Sp. gr. 0.85-0.92 (15° C.); M.P. 25°-28° C.; sol. pt. 17°-18°; sap. val. 171-192; iod. val. 56-59.

#### (f) LIQUID VEGETABLE NON-DRYING OILS

These do not absorb oxygen from the air, nor do they dry up. Iodine value usually under 100.

**Olive Oil**, much valued as an edible oil (salad oil), is obtained from the fruit of the olive tree. The cold pressed oil is the best; the second pressings or the



oil extracted by carbon disulphide is used for soap-making; consists of 70 per cent. triolein, 28 per cent. tripalmitin and tristearin, and a little linolein.—Sp. gr. 0.914-0.918; sol. pt. 2°-4° C.; sap. val. 190-195; iod. val. 79-93; Reichert-Meissl val. 0.6; Hehner val. 95; Maumené test, 41°-47° C.; refract. index, 1.47 (15° C.); viscosity, 312 secs. at 21° C. The fatty acids have sol. pt. 17°-26°; neut. val. 193; iod. val. 86-90.

**Olive-kernel Oil.**—Acid val. 2-3.5; sap. val. 182-188; iod. val. 79-88.

**Almond Oil**, obtained from bitter and sweet almonds, is very similar to **Peach-kernel Oil**, **Plum-kernel Oil**, etc.—Sap. val. 190-195; iod. val. 93-100.

**Arachis Oil, Pea-nut Oil, Earth-nut Oil**, is an edible oil obtained from the seeds of *Arachis hypogæa*. It contains arachidic acid as a glyceride.—Sap. val. 190-196; iod. val. 90-103; Reichert-Meissl val. 0.5; Maumené, 45°-75°; viscosity, 300-430 secs. at 21° C.; refract. index (15° C.) 1.47. The insol. fatty acids have sol. pt. 23°-28°; neut. val. 202; iod. val. 96-105.

**Croton Oil.**—Sap. val. 210-215; Reichert-Meissl val. 12-14; acetyl val. 38-41; iod. val. 101-109; sol. pt. 7° C. **Fatty acids** have neut. val. 201 and iod. val. 111-112.

**Grape-seed Oil.**—Acid val. 16; sap. val. 178-179; Reichert-Meissl val. 0.46-2.0; iod. val. 94-97. **Fatty acids** have neut. val. 187 and iod. val. 98-100.

**Castor Oil**, obtained principally from the seeds of *Ricinus communis*, consists mainly of the glyceride of ricinoleic, isoricinoleic, and dihydroxystearic acid, together with a little tristearine. It is a very viscous oil, miscible with absolute alcohol and glacial acetic acid in every proportion and much used as a medicine and lubricant, but also for manufacturing Turkey red oils (which see).—Sp. gr. 0.960-0.966 (15° C.); sol. pt. -10° to -12° C.; sap. val. 176-183; iod. val. 83-86; refract. index, 1.480 (15° C.); viscosity 1160 secs. at 37° C.; Reichert-Meissl val. 1.1. Mixed fatty acids, M.P. 13° C.; Maumené, 47.

**Blown Oils, Oxidised Oils, Soluble Castor Oils.**—When semi-drying vegetable oils, blubber oils, and liquid waxes are placed in a vessel provided with a steam heating coil, and warmed from 70°-115° C., while a current of air is blown through, the oils oxidise to viscid, dense fluids which are miscible with mineral oils. They form valuable lubricating oils, approaching castor oil in mechanical properties; since castor oil is insoluble in mineral oils (and so cannot be mixed with them), such oils are known commercially as "**Soluble Castor Oils.**"

**Turkey Red Oils, Sulphonated Oils** are viscous, transparent liquids used in the preparation of cotton fibre for dyeing and printing Turkey red. Concentrated sulphuric acid is slowly run, with constant stirring, into castor oil, the temperature being kept below 35° C. during the whole course of the reaction. The product is washed with water, settled, the lower layer drawn off and washed with a solution of Glauber's salt until only slightly acid; finally ammonia or soda is added until the sample will give a complete emulsion with water. Turkey red oil F. is completely soluble in water. Turkey red oil S. is only partially soluble in water. See p. 549.

**Nitrated Oils** are heavy, viscid liquids obtained by treating castor (or linseed) oil with a mixture of 2 parts of concentrated sulphuric acid and 1 part of concentrated nitric acid (sp. gr. 1.5). They form homogeneous mixtures with nitro-cellulose. Thus a product resembling ebonite is obtained by mixing 1 part of nitrated castor oil with 9 parts of nitro-cellulose. Dissolved in acetone, these nitrated oils form varnishes which are capable of enamelling leather and mixing paints.

For Bone Oil, see p. 420.

For Essential Oils, see p. 132.

For Rosin Oil, see p. 339.

For Oil of Turpentine, see p. 337.

#### (c) SEMI-DRYING VEGETABLE OILS.

These absorb oxygen from the air and become thick, without, however, completely drying up. Iodine value from 95-140.



**Cotton-seed Oil** is produced on an enormous scale in North America from the seeds of the various sorts of cotton trees; 17,000 tons, of value £580,000, were imported into Britain in 1910. It consists of glycerides of palmitic, oleic, and various unsaturated and hydroxy acids which cause the oil to somewhat rapidly oxidise at ordinary temperatures. It is, therefore, a weak drying oil. When cooled it deposits a large amount of cotton-seed stearin. Used as an edible oil, for adulterating lard, in the manufacture of margarine, soap, and lubricants.—Sp. gr. ( $15^{\circ}$  C.) 0.922-0.930; sol. pt.  $3^{\circ}$ - $4^{\circ}$  C.; sap. val. 191-195; iod. val. 105; refract. index, 1.478 ( $15^{\circ}$  C.); Maumené,  $74^{\circ}$ - $78^{\circ}$  C. Fatty acids have M.P.  $35^{\circ}$ - $38^{\circ}$ ; neut. val. 201-208; iod. val. 110-115.

**Test for Cotton-seed Oil.**—Dissolve 5 c.c. of the fatty acids from the oil in 2 c.c. alcohol in a test tube. Heat to boiling on water bath; add 2 c.c. of 2N.  $\text{AgNO}_3$  solution; an immediate black colour shows presence of cotton-seed oil. Five per cent. of cotton-seed oil can be detected in rape or olive oil by this test.

**Rape or Colza Oil, Sweet Oil**, obtained from the seeds of *Brassica campestris*, contains considerable quantities of rapic acid,  $\text{C}_{17}\text{H}_{32}\text{OH}\cdot\text{COOH}$ , and other unsaturated oxy-acids. Being cheap, it is much used for lubricating and edible purposes. The pure oil on exposure to air remains fluid for some days, but long exposure causes it to thicken somewhat and become rancid. If adulterated with drying oils it rapidly turns into a jelly-like mass, or even becomes solid.—Sp. gr. 0.914-0.918; sap. val. 170-178; iod. val. 94-107; Hehner val. 95; Reichert-Meissl val. 1 c.c.; viscosity, 330-380 secs. at  $21^{\circ}$  C., 91-94 secs. at  $60^{\circ}$  C.; Maumené test,  $60^{\circ}$  C. The elaidin test is here very useful for detecting presence of drying oils in rape oil. The fatty acids have sol. pt.  $13^{\circ}$ - $18^{\circ}$ ; neut. val. 185; iod. val. 96-104.

**Sesamé Oil**, obtained from the seeds of the sesamé plant, *Sesamum indicum* and *orientale*, is a valuable edible oil consisting of a mixture of the glycerides of stearic, palmitic, oleic, and linolic acids. To detect the presence of the oil, dissolve 0.1 g. sugar in 10 c.c.  $\text{HCl}$  (sp. gr. 1.19); add 20 c.c. of oil; shake and allow to stand: crimson colour in the aqueous filtrate shows presence of sesamé oil.—Sp. gr. ( $15^{\circ}$  C.), 0.914-0.916; sap. val. 188-195; sol. pt.  $-5^{\circ}$  C.; iod. val. 103-112; Maumené,  $65^{\circ}$ - $72^{\circ}$  C.; Reichert-Meissl, 0.7 c.c.

**Sunflower-seed Oil.**—Acid val. 0.2-6; sap. val. 190-193; iod. val. 118-136; Maumené,  $67^{\circ}$ - $75^{\circ}$  C. Fatty acids have sap. val. 201 and iod. val. 124-134.

**Maize Oil, Corn Oil.**—Obtained from germs of the maize plant, *Zea Mays*, L. The germs are a by-product in glucose and starch works using maize as their raw material. Acid val. 2-20; sap. val. 187-190; Hehner val. 88-94; Reichert-Meissl val. 0.3-10; iod. val. 113-129. Fatty acids have neut. val. 200 and iod. val. 121-127.

**Pumpkin-seed Oil** has acid val. 3.5-19; sap. val. 188-195; iod. val. 104-130.

**Black Mustard Oil** has acid val. 5-8; sap. val. 173-175; iod. val. 98-110.

**White Mustard Oil** has acid val. 5-6; sap. val. 170-171; iod. val. 92-96.

**Soja Bean Oil**, from the seeds of *Dolichos Soja*, L., *Soja hispida*, *Soja japonica*, etc., plants indigenous to Manchuria, Japan, China. The seed contains 18 per cent. oil and 30-40 per cent. protein, and yields 13 per cent. oil. The expressed meal is made into bean-cakes; the Soja bean industry being one of the most important of Manchuria and Japan, 1,500,000 tons of oil being exported in 1911. The oil consists of glycerides of oleic and linolic acids, dries on standing to a thin skin, and is used for edible and illuminating purposes in the Far East; now used as a paint and linoleum oil. See Toch, *Jour. Soc. Chem. Ind.*, 31, 572 (1912).—Sp. gr. 0.924; sap. val. 190-193; iod. val. 121-124; Maumené,  $59^{\circ}$ - $61^{\circ}$ ; sol. pt.  $+8^{\circ}$ - $15^{\circ}$  C. The fatty acids have a M.P.  $27^{\circ}$ - $29^{\circ}$ ; sol. pt.  $25^{\circ}$ ; iod. val. 115-122.



## (d) DRYING VEGETABLE OILS

These absorb oxygen from the air and dry up to a hard skin. They have an iodine value usually over 140.

**Hempseed Oil** has a sap. val. 190-195 and an iod. val. 140-166; Maumené, 95°-98°. Separated fatty acids have a sol. pt. 14°-16°; iod. val. 122-140.

**Candle-nut Oil** has a sap. val. 184-193 and an iod. val. 136-163.

**Niger-seed Oil** has a sap. val. 189-192 and an iod. val. 126-134. More important than these are the following:—

**Poppy-seed Oil**, a pale yellowish oil obtained by pressing from seeds of the poppy, is used as a salad oil and for making artists' paints: a good drying oil.—Sp. gr. (15° C.) 0.92-0.97; sap. val. 192-197; iod. val. 137-143; Reichert-Meissl val. 0.0; Hehner val. 95; Maumené test, 88° C.; refract. index, 1.477 (15° C.). Fatty acids have sol. pt. 16.5; neut. val. 199; iod. val. 139; refract. index, 1.451 (15.5° C.). The differentiation of poppy oil from walnut oil—*e.g.*, in the examination of white paints—is achieved most readily by the hexabromide test (which see); walnut oil yields 1.4-2 per cent. of hexabrominated glycerides, poppy-seed oil none.

**Walnut Oil**, a very good but expensive drying oil obtained from the seeds of the common walnut tree; being almost colourless, it is used for making the best white paints for artists, such paints being less liable to crack than those made from linseed oil. For distinction from poppy-seed oil see the latter. It is frequently grossly adulterated with mineral oil.—Sp. gr. 0.925-7 (15° C.); sap. val. 192-198; iod. val. 143-151; Maumené test, 96°-110° C.; Reichert-Meissl val. 0.0; Hehner val. 95. Fatty acids solidify at 16° C., and have iod. val. 150.

**Tung Oil, Chinese Wood Oil, Wood Oil**, a very important drying oil, possessing a characteristic odour and an even more pronounced drying power than linseed oil (giving, however, a *wax-like, non-elastic* product which renders it quite useless for paints in its ordinary condition), and when heated alone in absence of oxygen to 180°-250° C., it polymerises to a solid mass. It is said to be used for adulterating Chinese lacquers, and has been used in a solidified form for linoleum manufacture (see p. 50). In 1906 28,685 tons were exported from Hankow while the home consumption in China may amount to 60,000 tons. It is obtained from the seeds of *Aleurites cordata* and other trees growing in China, Japan, Tonkin, Annam, etc. It consists principally of glycerides of *oleic* and *elæomargaric acids*.—Sp. gr. 0.94; sap. val. 190-195; iod. val. 149-167; Maumené, 300°-372°. Separated fatty acids have sol. pt. 31°-37°; neut. val. 189; iod. val. 145-160.

## LINSEED OIL AND PRODUCTS DERIVED THEREFROM

**Linseed Oil**, a yellowish brown fluid from the seeds of the flax plant, *Linum usitatissimum*, is largely used for paint, varnish, oil-cloth, linoleum, and soft soap manufacture. The oil is principally composed of glycerides of unsaturated acids like isolinolenic acid (58 per cent.), linolenic acid (13 per cent.), linolic acid (13 per cent.), oleic acid (4 per cent.). The oil rapidly absorbs atmospheric oxygen, with formation of a tough resinous mass and hence is a "drying oil." This drying property is increased by heating to 180° C. or by the addition of metallic salts—"driers"; 38,000 tons, value £1,250,000, were imported into England in 1910.

**Constants of Linseed Oil**.—Sp. gr. (15° C.) 0.93-0.94; sap. val. 190-195; iod. val. 173-193; Reichert-Meissl val. 0.00; Hehner val. 95; Maumené test, 103°-145° C.; refract. index (15° C.), 1.4835; viscosity (21° C.), 212 secs. Flash-point about 243° C. (470° F.). **Mixed fatty acids** solidify at 13°-17° C.; melt at 17°-24° C.; neut. val. 196-199 and iod. val. 179-200.



To test the drying properties of linseed oil, smear a glass plate with the sample and expose in the water oven. Note how long it takes to dry, also the nature of the residuum; compare with a standard sample treated in the same manner.

To find presence of driers incinerate 50 g. in a large porcelain crucible and analyse residue for metals.

To find whether suitable for linoleum-making heat some in a copper basin to 260° C., stirring and blowing air through the mass. Dense fumes are evolved and after a time it becomes thicker. A specimen is drawn out and cooled. It should be "stringy," *i.e.*, capable of being drawn out into threads. Compare with a standard sample of oil treated similarly. Adulteration with mineral oils lowers the saponification value.

**The Chemistry of Drying Oils and Driers.**—When linseed oil and tung oil "dry", *i.e.*, harden, two distinct processes occur. Firstly, the oil thickens due to polymerisation of the fatty molecules. This may be brought about by the action of heat, *e.g.*, 260° C., in the case of linseed oil. Secondly, the oil is converted into a solid rubbery mass and later to a tough, hard film by an oxidation process. In this oxidation process, oxygen is added on across the unsaturated bonds of the glycerides. The polymerisation process is thought to be the most important one in the setting of paints containing linseed and tung oil. Although oxidation and polymerisation take place simultaneously during the drying of oils, we will consider each process separately for the sake of clarity.

**Atmospheric Oxidation of Fatty Oils.**—Linseed oil, either alone or more quickly in the presence of certain metallic salts called driers in the industry, will absorb oxygen from the air. This phenomenon is called the "drying" of oils, although, of course, no water is involved.

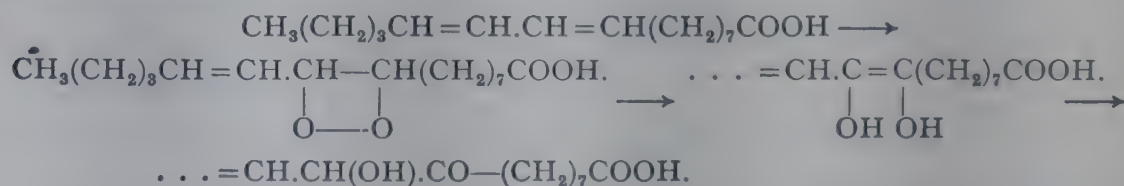
There is an induction period to the process, *i.e.*, oxygen is absorbed very slowly at first and then more rapidly, only slowing down when the absorption is nearing completion. When linseed oil is pure (*i.e.*, no driers are present) the induction process takes about three days, and the whole process about 30 days. At 100° C. the induction period may be about half an hour, and the process may be complete in 7 hours.

When 0.1 to 0.3 per cent. of a drier is added, *e.g.*, lead manganese or cobalt salts especially, naphthenates, resinates or linoleates, the oxidation period is greatly shortened. This has been found to be due mainly to the elimination of the induction period. Oxidation then takes place to completion at its maximum rate.

The oxidised linseed oil is often called linoxyn, which is quite often also the name given to the complex mixture present in the film obtained after oxidation of linseed oil. This contains unsaturated glycerides which have partially or completely undergone change by the addition of a molecule of oxygen to unsaturated bonds, together with decomposition products, some of which are volatile and are finally lost to the atmosphere.

Other drying oils do not give a satisfactory film on drying. One of the essential characteristics of a drying oil for use in the paint industry is that the film formed should be tenacious and flexible. Linseed oil fulfils these two criteria satisfactorily.

It is thought that the initial product when linseed oil dries is of the nature of an organic peroxide. This can indeed be shown by liberation of iodine from acidified potassium iodide solution. The final product appears to contain little peroxide. The work of Fahrion, Ellis, Morrell and Marks during the last twenty years indicates that the following change takes place. A peroxide is formed across the double bond of the linoleic acid group which isomerises into an  $\alpha$ -hydroxyketone thus:



Morrell and Marks actually worked with  $\alpha$ -elacostearic acid, which contains three double bonds. They found that the third bond, furthest from the  $-\text{COOH}$  group, did not oxidise, and that the second furthest oxidised, but was unstable and basic in character, whereas the double bond closest to the  $-\text{COOH}$  group was acidic and isomerised to an  $\alpha$ -hydroxyketone group. The second group did not do this, but readily took part in polymerisation reactions. This work suggests that the basic "second double" bond oxidation is the one that takes the predominant part in the polymeric hardening of linseed oil.

The induction period in the hardening of linseed oil is thought to be due to natural antioxidants present in linseeds, for synthetic materials, such as hydroquinone, can be introduced which further retard the drying of linseed oil. The function of metallic oxides, salts and other driers is now believed to be one of destruction of the natural antioxidants in linseed oil and more than a catalytic oxidation action. Nevertheless we have the following two facts in support of a catalytic action:—

1. A very small quantity of a drier is required to cause drying of a very large quantity of oil.
2. The best driers are highly oxygenated compounds, especially those which exist in various stages of oxidation—*i.e.*, can change from stage to stage, taking oxygen from the air to become



highly oxidised and then giving "nascent oxygen" up to the oil. Examples of these are manganese dioxide and salts of manganese, red lead and salts of lead.

In the accompanying table \* a list is given of the common driers, together with the percentage of metal usually found in them. The theoretical percentage of metal cannot always be given, as the composition of the finished product varies according to circumstances, the amount of water of crystallisation in particular being dependent upon the temperature at which the salts are prepared.

TABLE OF COMMON DRIERS.

Name.	Colour.	Per Cent. Metal in Pure Drier.	Per Cent. Metal in Commercial Drier.
Litharge - - - - -	Buff - - -	90.3	89.4
Red lead - - - - -	Red - - -	90.1	86.7-87.6
Lead acetate - - - - -	White - - -	54.6	52.4-53.3
„ linoleate - - - - -	Brown - - -	...	31.2
„ oleate - - - - -	Yellow - - -	...	22.6
„ rosinate (fused) - - - - -	Yellow-brown - - -	...	15.6
„ „ (ppted.) - - - - -	Light brown - - -	...	...
Manganese borate - - - - -	Pinkish- - -	...	7.8-23.8
„ carbonate - - - - -	Buff - - -	...	38.8-42.6
„ dioxide- - - - -	Black - - -	63.2	50.4-54.3
„ hydroxide - - - - -	Brown - - -	...	46.5
„ linoleate - - - - -	Dark brown - - -	...	7.8-8.9
„ oleate- - - - -	Brown - - -	...	8.1
„ oxalate - - - - -	Pinkish- - -	...	30.2
„ rosinate (fused) - - - - -	Dark brown - - -	...	2.3-3.5
„ „ (ppted.) - - - - -	Pinkish- - -	...	5.0-6.1
„ sulphate (anhydrous) - - - - -	Pinkish- - -	36.4	...

As is evident from the above table, a considerable variety of substances are placed under the category of driers. In the case of the metallic salts the efficiency is influenced to a slight extent by the nature of the acids with which the metal is combined. If this latter is favourable to the catalytic action, the drier is slightly more powerful than might otherwise be expected. This is true of rosinic acid, and metallic rosinates have of late found great favour amongst painters generally. They may be prepared by fusing together rosin and a metallic oxide, a product free from moisture being obtained, and known as a "fused" drier. "Precipitated" driers, as their name implies, are obtained by mixing solutions of alkaline rosinates with a soluble metallic salt, whereby the drier is precipitated. Such driers always contain a considerable quantity of moisture, up to, say, 6 per cent., and are thereby readily distinguished from fused driers. Other organic salts, such as the oleates and linoleates of lead and manganese, are also very efficient driers. Lewkowitsch has recently prepared tungates of these metals from the fatty acids of tung oil.

Since these organic compounds are readily soluble in turpentine and linseed oil, they are known as "soluble" driers. Solutions in either or both of these solvents are termed "liquid" driers or terebines.

It does not always follow, however, that the most powerful driers are necessarily the best for all work; other properties should be taken into consideration. For example, lead acetate is well known to be weaker than red lead and litharge, nevertheless it is used extensively in the manufacture of patent driers because it does not darken the oil so much—a point of considerable importance when white and light coloured pigments are being used. Ferrous sulphate should be used with care as it tends to render the film of oil brittle.

Now, according to the catalytic theory, chemically inert substances cannot be expected to function as driers. Nevertheless Hurst † found one "patent" drier to contain more than half its weight of calcium sulphate, whilst another contained 77 per cent. of barium sulphate (barytes) and silica. It would be unwise, with our present limited knowledge, to assume that chemically inert bodies are necessarily useless as driers, for it may well happen that the introduction of fine particles of solid into the oil can assist in some physical manner the absorption of oxygen, just as we know fine powders can greatly accelerate the oxidation of combustible gases. At present the only method of determining whether or not a drier is of any value is to test it experimentally in some such manner as that indicated below.

\* This table is taken from Friend's "Introduction to the Chemistry of Paints," p. 155, the data having been calculated from the results given by T. A. Davidson in his paper entitled "The Action of Driers on Linseed Oil," read before the Paint and Varnish Society, 12th November 1908.

† See "Painters' Colours, Oils, and Varnishes," by Geo. Hurst (Griffin & Co., 1906), p. 437.



Turpentine is not infrequently regarded as a drier, but the researches of W. N. Hartley would seem to indicate that such is not the case in the strictest sense of the term. Turpentine assists in the drying of the oil by rendering it thinner, so that the painter can spread it over a larger surface, and thus come into contact with a proportionately greater quantity of air. It is not impossible, however, that whilst the above is the main function of the turpentine, a catalytic action does take place to a small extent in addition, for it is well known that turpentine readily absorbs oxygen from the air, yielding, as many chemists believe, an organic peroxide, which latter would act on the oil in an analogous manner to an inorganic peroxide.

In the case of litharge and red lead, complications arise owing to tendency which these oxides exhibit to saponify the oil, whereby an insoluble lead soap is produced, which produces a more brilliant coat on drying than the pure oil alone. To what extent this saponification assists the rate of drying is at present unknown.

**Practical Testing of Driers.\***—The old method of testing driers by noting the time taken by a thin film of terebine to set hard on glass cannot be too strongly condemned, for it leads to most conflicting results. One of the most satisfactory methods is that given by T. A. Davidson.† This investigator prepares a series of mixtures of linseed oil and drier in varying proportions. These are kept at a uniform temperature for a number of hours in separate stoppered bottles. The liquids are now filtered through paper into fresh bottles, and a portion of each is run on to a glass slide and placed in an air oven at constant temperature. From time to time the slides are examined and the number of minutes or hours noted that are required before the film is sufficiently firm to bear the finger being gently drawn across it without leaving a whitish mark. This time is known as the "setting value," is greatly affected by a number of factors, such as temperature, rate of change of air, thickness of the oil film, moisture, and the nature of the surface to which the oil is applied. In testing a drier, therefore, it is necessary to perform two series of experiments at the same time and under precisely similar conditions, one with a standard drier, whose efficiency is well known from practical experience; the other with the sample to be tested. Only in this way is it possible to arrive at satisfactory and reliable results.

### Varnishes, Lacquers, and Enamels

Varnishes, lacquers, and enamels, when applied to the surfaces of bodies, have in general two functions to fulfil, namely, those of protection and of ornamentation.

**Oil Varnishes** were first manufactured on a commercial scale in England at the close of the eighteenth century, and are prepared by dissolving resins in linseed oil. Owing to the fact that the resins are, as a rule, insoluble in the oil before fusion, varnishes cannot be prepared by simply mixing the ingredients at the temperature of the room. The resins are first fused in copper gum pots, and a quantity of oil already at 500° F. (260° C.) is added under vigorous stirring. The contents of the pot are now run into a large iron tank capable of holding the "runnings" of several pots, and the temperature maintained at 500° F. until the varnish has cleared and is stringy. It is then cooled, thinned with turpentine, and stored to clear and age.

Simple as the above process appears to be in theory, years of practice are required to produce thoroughly satisfactory results. If the resin is not properly fused it cannot undergo thorough union with the oil, the imperfectly fused portions remaining suspended as very fine insoluble particles in the varnish, instead of being dissolved in the same. The result is that when the varnish is applied to any surface it sets with a "bloom." Whilst this is not the only cause of blooming it is a sufficiently common one to merit attention.

For pale varnishes it is essential that the resins employed be pale, and, unless the temperature of the gum pot is carefully watched and maintained as low as possible, the resins will darken and spoil.

These technical difficulties, coupled with the fact that the already costly resins lose from 5-20 per cent. in weight during fusion, has led to many attempts on the part of manufacturers to employ some other method. Experiments have been

\* This subject is dealt with in further detail in Friend's "Introduction," etc., p. 161 *et seq.*

† Davidson, *loc. cit.*



carried out with terpineol, with amyl alcohol, and with naphthalene and phenols as solvents, but with doubtful success.

**Enamels** consist of oil varnishes into which certain finely levigated pigments, such as zinc oxide and venetian red, have been thoroughly ground. Black enamels are usually prepared from asphaltum.

**Spirit Varnishes** are prepared by mixing resins with such solvents as methylated spirit or turpentine, and allowing to stand in a warm place. Excessive heat must be avoided, owing to the volatile nature of the solvents, and the inflammability of their vapours. The methylated spirit employed should not be weaker than 64 over proof.

**Nitro-cellulose Varnishes.**—Varnishes used in the manufacture of artificial leather and in special lacquer work consist of nitro-celluloses dissolved in amyl acetate and suitably coloured. Large quantities of amyl acetate are annually employed in various industries for making such nitro-cellulose varnishes. These varnishes are likewise used for painting iron work owing to their non-porous nature. For particulars see pp. 216*a*, *b*, and *c*.

**Water Varnishes** are made by dissolving gums or glue in water. If, just before use, a small quantity of potassium bichromate is added to glue varnish, the coat is rendered almost waterproof.

**Natural Varnishes.**—Two genera of plants belonging to the *Anacardiaceæ* yield a sap on tapping, which is used in the Far East as a natural varnish or lacquer, namely, *Rhus* for Japanese and Chinese lacquers, and *Melanorrhæa*, which yields black Burmese varnish. Japanese lacquer is hard, its hardness increasing with age. Its great value lies in its persistent lustre, and to the resistance which it offers to such agencies as spoil our ordinary oil varnishes. It should be borne in mind that the so-called lac ware of India is not true lacquer ware, as it is produced by the aid of shellac dissolved in suitable liquid menstrua. The chief Chinese tree yielding lacquer is *Rhus vernicifera*, native to that country, and, like the art of lacquering, introduced from China into Japan. Chinese lacquer is frequently adulterated with tung oil. When first obtained from the tree it is greyish white in hue, but quickly oxidises and becomes brownish black. The Japanese lacquer is very similar. Both lacquers harden only in a moist atmosphere, hence in China lacquering is performed in wet weather, and in Japan it is conducted in special moisture-laden rooms. Oxygen is slowly absorbed during the setting to the extent of 5.75 per cent. of the weight of the original varnish. The only methods of thinning the lacquer known to the Japanese are by warming, or by addition of camphor. For this reason camphor wood is not used as the foundation for lacquer, although almost any other kind of wood may be employed.

**Synthetic Varnishes.**—See under Plastics (p. 619).

## Solidified Linseed Oil, Linoxyn, Oil Cloth and Linoleum

### LITERATURE

See REID, *Journ. Chem. Soc. Ind.*, 1896, 75.

INGLE, *loc. cit.*, 1904, 1197.

A. DE WAELE and O. J. PATRICK, "Linoleum": Its Manufacture and Valuation, *loc. cit.*, 1915.

The technical literature is poor, and much of the materials for the accompanying article were privately communicated by firms interested in the trade.

Linseed oil rapidly takes up oxygen and solidifies to a flexible solid mass of unknown constitution, termed "solidified linseed oil," "oxidised linseed oil,"



"linoxyn," etc. The substance is manufactured on a large scale by several different processes (F. Walton, 1860-63).

1. Linseed oil, freed from moisture by settling (sometimes by filtering through dry salt)—otherwise frothing ensues on boiling—and boiled with a drier to accelerate oxygen absorption, is allowed to flow down a light cotton fabric ("scrim") suspended from the ceiling of a high room which is maintained at 38° C. The flooding with oil takes place daily, and each layer solidifies in about twenty-four hours. The process is continued for six to eight weeks, the oil dripping from the cloth being drawn off and allowed to flow again down the cloth. When the layer of solidified linseed oil is half an inch thick, the "skins" (25 ft. long) are cut down, and the mass passed between rollers. It is known as "scrim oil." The scrim at first supports the oil, but before the skins are ready to be cut down the cotton is so thoroughly rotted that it readily disintegrates, and cannot be traced in the subsequent processes through which the oil passes.

2. Raw linseed oil is placed in a horizontal steam-jacketed cylinder within which a central shaft provided with arms rotates with high velocity. The cylinder is only half filled with oil, and the arms beat it up into a fine spray, while at the same time a current of air is driven through. Steam in the jacket is maintained so as to heat the oil to a proper temperature (which differs with the kind of oil to be produced). As the oxidation proceeds the temperature rises, and the steam is now replaced by cold water. The oil is oxidised in five to six hours, but if an oil of a light colour is required, twenty-four hours is required. The thick viscous liquid is run while hot into trays where it solidifies on cooling. At this stage it is not so thoroughly oxidised as scrim oil, and (except when used for cork carpet) the trays have to be kept in stoves at a temperature of about 38° C. for from four to eight days until the desired degree of oxidation is obtained.

In this forced method of oxidation there is a loss of about 8 per cent., whereas, in the natural oxidation of the scrim method there is an actual gain of about 7 per cent. The oil oxidised in this manner is more liable to spontaneously ignite than that produced by the scrim process. The oil is not quite so elastic as that prepared by the "scrim" process, owing to part of the oxidised oil being "superoxidised" to a liquid substance, first discovered by Reid.

3. A third process for reducing linseed oil to a thick mass suitable for mixing with ground cork, etc., for linoleum making is achieved by prolonged boiling alone, which causes the oil to polymerise. A considerable proportion of the linoleum sold at the present day is made from oil so prepared. The manufacture of linoleum from polymerised linseed and tung oil has been patented by Dewar and the Linoleum Manufacturing Company (English Patent, 5,789, 1903). See p. 45.

#### LINOLEUM AND OIL-CLOTH MANUFACTURE \*

The first step in the manufacture of linoleum is the production of "linoleum cement." This is done by melting the solidified oil with various gum resins (usually kauri gum and rosin), and mixing with it cork flour and various pigments and fillers. The linoleum composition thus obtained is finally rolled on to canvas. A good elastic cement is composed of about 8½ cwt. of oxidised oil, 1 cwt. rosin, and 3 cwt. kauri gum; sometimes copal is added. Each manufacturer, however, uses his own formula, and this is carefully kept as a trade secret. The kauri is pulverised, but the rosin can be used in lumps since it acts as a flux. The mixing operation is carried out in a steam-jacketed vessel provided with stirrers. Samples are withdrawn from time to time and tested. It is of the greatest importance that no overheating takes place. When thoroughly mixed, the "cement" is run into pans, and in summer is sometimes artificially cooled, since large masses of this (as well as the oxidised oil) have been known to heat and spontaneously inflame. The cement is cut into small pieces, mixed with rather more than its weight of ground cork, passed through steam-heated mixing rolls, more thoroughly amalgamated in a

\* See Reid, *Journ. Soc. Chem. Ind.*, 1896, 75; Ingle, *loc. cit.*, 1904, 1197.



mixing drum (various colouring matters being here added according to the colour desired for the finished linoleum) and then passed into a "German"—an apparatus resembling a large sausage machine, but very strongly made. At first steam heating is necessary, but once the machine is working the heat generated by friction keeps the mass soft, and in summer it is even necessary to circulate cold water in the jacket instead of steam. From the "German" the linoleum issues as lumps or pellets, and is passed through mixing rolls, in which it is converted into sheets, and finally is rolled upon jute canvas by means of steam-heated rolls. The canvas back is protected by a varnish ("backing") spread upon it by means of a special machine; the main ingredients of the backing are oxidised oil and varnish, or varnish bottoms mixed with ochres or oxides; the material is fluid when hot, but solidifies on cooling. Finally the linoleum is "seasoned" in rooms at 23.5° C., best in horizontal racks.

Linoleums may be grouped into (1) Plain and Printed; (2) Inlaid; (3) Cork Carpets.

The **Plain Linoleums** consist essentially of cork, pigment, and cement rolled on canvas; they are printed with oil colours so as to produce designs ("**printed linoleums**"). The oil paints, however, in time wear off, and efforts were made to produce coloured patterns running right through the thickness of the coating composition, thus introducing "**inlaid linoleums.**" This requires special machines of extreme ingenuity. The modern machine is continuous and practically self-operating and may deal with as many as 90,000,000 separate units of the cement pattern per day. Differently coloured linoleum compositions are granulated and moulded into the required shapes, and placed upon the canvas in such a way as to produce the required design; an alternative method is to roll the differently coloured compositions into sheets, and cut from these sheets various forms and stamp them upon the canvas. The patterns thus built up are immediately welded together by heat and pressure, and afterwards seasoned. Details of these special processes will be found in the patent literature. All inlaid linoleums contain a large proportion of wood flour in addition to cork dust.

**Granite Linoleums** are of this class. The "granite" effect is produced by mixing together granules of differently coloured linoleum compositions before pressing the material on to the canvas. In these inlaid linoleums the proportion of cement is generally rather more than that of cork and wood flour, so as to ensure a thorough welding of the various linoleum compositions forming the design.

In **Cork Carpets** the cork grains are larger, and wood dust is never employed, while the quantity of pigment is usually smaller than in the plain and inlaid varieties. Both kinds of cement are used.

**Oil-cloth** consists simply of fabrics coated with linseed oil, whiting, and pigment, and are printed in oil colours in the usual way.

The colours used in linoleum and oil-cloth manufacture are—

*Red.*—Red oxides, or, in the case of bright inlaid colours, permanent lakes.

*Blue.*—"Ultra" blue.

*Green.*—Chrome green and Brunswick green.

*White.*—White lead, lithophone.

*Yellow.*—Chromes.

*Black.*—Vegetable black.

The authors' best thanks are due to Mr A. H. Dewar, F.R.I.C., manufacturing manager of the Linoleum Manufacturing Co. Ltd., who gave us much information regarding the modern methods used in manufacturing linoleum.

**Statistics.**—The amount of oil-cloth and linoleum imported into the United Kingdom in 1910 was 1,060,000 sq. yds., of value £71,700. The amount exported is shown by the following figures:—



	Quantities.		Value in 1910.
	1906.	1910.	
Oil-cloth—			£
For floor coverings - - - Sq. yds.	37,395,100	36,123,800	1,932,742
For furniture coverings - - - „	8,206,200	15,773,700	611,602
For all other purposes - - - „	3,272,700	2,394,800	87,297
Total of oil-cloth - - - „	48,874,000	54,292,300	2,631,641

The United States in 1910 imported 4,800,000 sq. yds. (value, \$1,834,000) of oil-cloth and linoleum; the export of floor oil-cloth reached \$128,000 in 1910, the value of other kinds of oil-cloth exported being returned as \$353,000.

For modern statistics see Appendix III.

## ANIMAL AND VEGETABLE WAXES (NON-GLYCERIDES)

### LITERATURE

See under Oils, Fats, and Waxes. Special works dealing with waxes alone are—

L. SEDNA.—“Das Wachs und seine technische Verwendung.” Vienna, 1902.

T. W. COWAN.—“Wax Craft: All about Beeswax.” London, 1908.

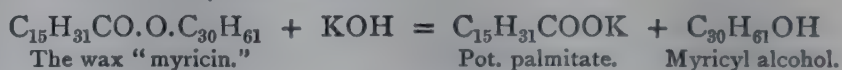
The manufacture of ordinary commercial “sealing wax” (which usually does not contain true wax) is dealt with in the following works:—

H. C. STANDAGE.—“Sealing Waxes.” London, 1902.

L. E. ANDÉS.—“Siegel- u. Flaschenlacke.” (Vienna, 1885).

W. ELLRAM.—“Siegel- und Flaschenlackfabrikation.” Lodz, 1900.

The waxes are esters formed by the union of fatty acids and alcohols not belonging to the glycerol series. Hence waxes are sharply distinguished from fats in that they contain no glycerol; they have, however, many properties in common with true glycerides (fats); thus they can be saponified with alkalies, the salts of fatty acids and alcohols being obtained:—



The saponification is much more difficult to carry out in the case of waxes than in the case of fats. Wool wax, for instance, must be boiled with alcoholic potash for at least twenty hours; moreover the higher alcohols, being insoluble in water, occur in the “unsaponifiable” residue. This allows us to readily distinguish fats from waxes; for whereas most fats yield 95 per cent. of fatty acids, the liquid waxes yield only 60-66 per cent., the remaining 40-34 per cent. being made up of monovalent alcohols, among which we may mention:—

Ethane series. $\text{C}_n\text{H}_{2n+1}\text{OH}$ .	Cetyl alcohol - - -	$\text{C}_{16}\text{H}_{33}\text{OH}$ .	Aromatic alcohols.	Lanolin alcohol -	$\text{C}_{12}\text{H}_{25}\text{OH}$ .
	Octodecyl alcohol -	$\text{C}_{18}\text{H}_{37}\text{OH}$ .		Cholesterol -	$\text{C}_{27}\text{H}_{45}\text{OH}$ .
	Carnaübyl „ -	$\text{C}_{24}\text{H}_{49}\text{OH}$ .		Isocholesterol -	$\text{C}_{27}\text{H}_{45}\text{OH}$ .
	Ceryl „ -	$\text{C}_{26}\text{H}_{53}\text{OH}$ .		Phytosterol -	$\text{C}_{27}\text{H}_{45}\text{OH}$ .
	Myricyl „ -	$\text{C}_{30}\text{H}_{61}\text{OH}$ .		Sitosterol -	$\text{C}_{27}\text{H}_{45}\text{OH} \times \text{H}_2\text{O}$ .
	Psyllostearyl „ -	$\text{C}_{33}\text{H}_{67}\text{OH}$ .			

### Liquid Waxes

**Sperm Oil**, from the blubber and head cavities of the sperm whale, consists of combinations of unknown\* alcohols with fatty acids. Cooled to low temperatures the oil deposits **spermaceti** (which see). The oil is a valuable lubricant, especially for rapidly running machines; since it does not become gummy or rancid it can be used for delicate machinery such as watches. It retains its viscosity at high

\* Hilditch (1941) says certain saturated and unsaturated alcohols containing  $\text{C}_{16}$ ,  $\text{C}_{18}$  or  $\text{C}_{20}$ .



temperatures. Sperm oil is used for lubricating, illuminating, dressing leather, and tempering steel.—Sp. gr. ( $15^{\circ}$  C.), 0.880-0.883; sap. val. 123-133; iod. val. 81-84; Reichert-Meissl val. 0.60; fatty acids, 60-64 per cent.; alcohols, 37-41 per cent.; Maumené test,  $45^{\circ}$ - $51^{\circ}$  C. If adulteration with fatty acids has taken place glycerol will be found present. The percentage of glycerol multiplied by 10 will give the percentage of fatty oil.

**Doegling or Bottlenose Oil** is a fluid very similar to sperm oil, with almost identical constants; it can be distinguished from sperm oil by its taste. It has a lower price than the former oil on account of a slight tendency to "gum."

### Solid Animal Waxes

**Spermaceti**, the white crystalline wax which separates from chilled sperm oil, consists principally of cetin (cetyl palmitate),  $C_{16}H_{33}O.CO.C_{15}H_{31}$ . The substance is a good candle material.—Sp. gr. 0.90-0.96 ( $15^{\circ}$  C.), 0.80-1.81 ( $100^{\circ}$  C.); sol. pt. and M.P.  $44^{\circ}$  C.; sap. val. 125-134; iod. val. 3.8; alcohols, 51.4 per cent.; fatty acids, 53 per cent.

**Beeswax\*** is obtained from the honeycomb of bees by melting, straining from impurities, and running into moulds. Sometimes the wax is expressed. It may be bleached by exposure to sunlight, or by an oxidising agent such as nitric acid, chromic acid, or hydrogen peroxide. The ordinary yellow wax smells of honey, the bleached is white, inodorous, and tasteless, consisting mainly of myricyl palmitate,  $C_{30}H_{61}O.C_{16}H_{31}O$ , and cerotic acid,  $C_{26}H_{52}O_2$ .—Sp. gr. 0.962-0.975 at  $15^{\circ}$  C., 0.81-0.83 at  $100^{\circ}$  C.; sol. pt.  $60^{\circ}$ ; M.P.  $63^{\circ}$  C.; acid val. 20; sap. val. 90; iod. val. 8-11; refract. index,  $43^{\circ}$ - $45^{\circ}$  (butyro-refractometer); fatty acids, 47 per cent.; unsaponifiable matter, 55 per cent.; Reichert-Meissl val. 0.3-0.5.

**Insect Wax, Chinese Wax** is obtained from an insect, *Coccus ceriferus*, Fabr., or *Coccus pela*, Westwood, which deposits the wax on certain trees. A hard, yellowish-white solid consisting mainly of ceryl cerotate,  $C_{26}H_{51}O.CO.C_{25}H_{51}$ . This body is used as a furniture and leather polish, for sizing paper and cotton goods, and as a candle material.—Sp. gr. 0.92-97 at  $15^{\circ}$ , 0.81 at  $100^{\circ}$  C.; M.P.  $81^{\circ}$ - $83^{\circ}$  C.; sap. val. 80-93; iod. val. 1.4; fatty acids, 51 per cent.; alcohols, 49 per cent.

**Wool Wax, Wool Grease** is the natural grease encrusting sheep's wool fibre. Before spinning, this grease is removed, sometimes by extracting with volatile solvents, but more usually by washing with soap and sodium carbonate solutions, with which the oil forms an emulsion; on adding sulphuric acid to this the grease separates. Since the process of wool washing gives rise to very large volumes of waste liquors containing much free and combined fat, complications ensue when these liquors are run off into sewers. In the case of Bradford £12,000 per annum is expended for sulphuric acid with which to separate the fatty matter from the sewage.† The recovered fatty acids are sold under the name **Yorkshire grease** or **Wakefield grease** at £6 per ton, and 40 tons per week are recovered from the sewage. In large wool-washing works the suds are treated before running to waste, the grease being converted into lanolin, soap, and lubricating oil. In a works of moderate size 50 tons of grease are obtained monthly, and sold at £9 to £10 per ton.

The crude grease thus obtained is purified by various patented processes, and brought into the market under the name "**lanolin**." Owing to the ease with which wool wax is absorbed by the skin it forms the basis of many valuable ointments and cosmetics. The chemical composition of wool wax is not exactly known; besides glycerides it contains stearic and palmitic ethers of cholesterol and ischolesterol,

\* A complete account of beeswax, its manufacture and properties, is given by T. W. Cowan, "Wax Craft: All about Beeswax." London, 1908. See also W. F. Reid, *Journ. Soc. Arts* (1903), 522.

† *Jour. Chem. Ind.* (1909), 38, 14.



**Summary.**—The following tables, taken from A. C. Wright's "Analysis of Oils," summarise the chief chemical and physical properties of the better known oils:—

THE CHEMICAL PROPERTIES OF

	Acid Value.*	Saponification Value.	Hehner Value.
<b>Drying oils—</b>			
Linseed oil - - - - -	1-8	187-196	94.8
Hempseed oil - - - - -	1	190-195	...
Wood oil - - - - -	0.7-10.7	(155-) 190-197	96.0-96.6
Candle-nut oil - - - - -	...	184-192.6	95.5
Walnut oil - - - - -	10	192-197	95.4
Poppy-seed oil - - - - -	4-11	189-198	95.0
Niger-seed oil - - - - -	5-12	189-192	94.1
<b>Semi-drying oils—</b>			
Sunflower-seed oil - - - - -	0.2-6	190-193	...
Maize oil - - - - -	2.2-20	187-190	88.2-93.6
Pumpkin-seed oil - - - - -	3.5-19	188-195	96.2
Sesamé oil - - - - -	0.2-8	188-192	95.6-95.8
Cotton-seed oil - - - - -	0.4-2.2	190.4-197	94.2
Rapeseed oil - - - - -	1.4-4.0	(169.4-) 173-178 (-181)	94.5-96.3
Black mustard oil - - - - -	5.7-7.4	173-175	96.0
White mustard oil - - - - -	5.4	170-171	95.8
<b>Non-drying oils and solid fats—</b>			
Earthnut oil - - - - -	0.3-33	185.6-196	95.6
Almond oil - - - - -	10	188-195	96.6
Croton oil - - - - -	...	210.3-215.6	...
Grapeseed oil - - - - -	16	178-179	...
Castor oil - - - - -	0.4-0.8	173-183	...
Olive-kernel oil - - - - -	2.0-3.5	182.3-188	...
Olive oil - - - - -	0.6-5.0 (-25)	185-195	0.6
Ben oil - - - - -	...	...	...
Neat's foot oil - - - - -	0-0.7	194-197.4	95.3-95.5
Lard - - - - -	...	195.3-196.6	95.8-96.15
Lard oil - - - - -	0.4	193	97.4
Mahwa butter ( <i>Bassia latifolia</i> ) - - - - -	4.8-70.8	187-194	94.7, 95.0
Mowrah-seed oil ( <i>Bassia longifolia</i> ) - - - - -	...	188.4	...
Palm oil - - - - -	...	196-202	...
Bone fat - - - - -	...	172-194	86-94
Tallow (beef) - - - - -	...	193-198	95.6
Tallow (mutton) - - - - -	...	195	95.5
Tallow oil - - - - -	...	197	...
Cocoa (cacao) butter - - - - -	1.1-4.5	191.8-194.5 (-200)	...
Vegetable tallow - - - - -	...	198.5-203.6	...
Butter fat - - - - -	0.2-0.6	221-235	86.0-88.8
Palm-kernel oil - - - - -	...	246-250	...
Japan wax - - - - -	11-32	(206-212-) 217-222 (-237.5)	90.6
Myrtle wax - - - - -	3	205.7-211.5	...
Cocoa-nut oil - - - - -	10.0-35.2	255-263	82.3
<b>Marine animal oils—</b>			
Menhaden oil - - - - -	0.2	185-192	...
Sardine oil - - - - -	2.2-21.7	189.8-193.8	94.5-97.1
Cod-liver oil - - - - -	0.3-31.9	(171-) 175-188	96.5
Seal oil - - - - -	0.8-43.1	(178-) 189-193	95.4-96.0
Whale oil - - - - -	0.3-51.4	184-200 (-224)	...
Porpoise oil - - - - -	0.8	203.4-218.8	...
Dolphin oil - - - - -	...	197-290	66.3-93
<b>Liquid waxes—</b>			
Sperm oil - - - - -	0.4	(117-) 125-133 (-147)	...
Arctic sperm (bottlenose) oil - - - - -	...	123-133	...
<b>Solid waxes—</b>			
Spermaceti - - - - -	0.1-5	(108) 122.7-136	...
Beeswax - - - - -	17.5-21	87.5-99	...
Carnaúba wax - - - - -	4-8	79-95	...
Wool wax - - - - -	0.6-1.8	83-102.4	...

NOTES (see also the notes appended to the Table of Physical Properties, p. 59).

\* The acid values frequently vary greatly; in most cases the higher value given is not to be regarded as a superior limit.

† The total volatile (soluble) acids may be calculated from the difference between the apparent and true acetyl values determined by Lewkowitsch's method, given in the next column. This difference, multiplied by  $\frac{5}{5.6}$ , gives (very nearly) the number of c.c. of decinormal potash required to neutralise the volatile acids contained in 1 g. of the fat.



# THE OILS, FATS, AND WAXES.

Reichert-Meissl Value.†	Acetyl Value (Lewkowsch's Method).		Iodine Value.‡	Insoluble Fatty Acids.	
	Apparent.	True.		Saponification Value.	Iodine Value.‡
0 (?)	12.5	11.7	(160-) 170-202	182-199	170-180 (?)
...	...	...	(140-) 155-166	...	141 (?)
...	...	...	150-170	(168)-189	(144-) 150-160
...	...	9.8	(136-140) 163.7	...	142.7-144
0	...	...	143-148	...	...
0	...	...	(120-) 128-137	...	139
0.1-0.6	...	...	126.6-134	...	...
...	...	...	118-132 (-136)	201.5	124-134
4.2-9.9	...	...	(113-) 118-128.6	200.0	121-126.4
...	...	...	113-130.7	...	...
0.35	...	...	104.8-110.4	195-199	109-112
...	7.7	7.6	(97.5-) 102.5-110	201-208	102.4-115
0.0-0.8	...	...	(94-) 98-105 (-110)	174-182	98-105
0	...	...	98.8-106 (-110.5)	...	110
0	...	...	92-96.7	...	96
0	...	...	(82-) 92-105	198	96-103.4
0	...	...	93-102	...	...
12-14	38.6-40.8	...	101-104.7	201	111.2-111.8
0.46	...	...	94-96.2	187	98-99
...	...	146.9	82.6-87	182-193	86.6-94
...	...	...	81.8-87.8	...	...
...	...	...	78-85 (-88)	196-200	86-90
...	...	...	80-84	...	...
...	...	...	67-72.9	200.6-201.2	(63.6-69.5) 74.5-75.8
...	...	...	55-63 (-68.8)	...	59.0-63.5
0	...	...	73-77.3	...	...
0.4-0.9 (1.23)	...	...	(29.9?) 53.4-67.8	206.0	(31.6?)
...	...	...	50.1	...	...
0.5	...	...	50-53.5	205-213	53
...	...	...	46-56 (-62)	201-206	55-57
0.5	6.6	4.6	} average, 41-46 {	196-207	41
...	...	...		...	37.8
...	...	...	71.0-75.7	...	54.6-57
0.2-0.8 (-1.6)	2.8	2.0	32-37.0 (-41)	198	39.1
...	...	...	28-38	202-209.5	30.3-39.5
(11.2-) 24-33 (-41)	...	...	29-37	212.5-217	28-31
5	...	...	10-17	258-265	(3.6-) 12-13.6
(4.7-6 per cent. of soluble acids)	...	...	8.3-12.8	211-216	10.6
...	...	...	10.7	230	...
6.6-8.5	...	...	8.2-9.6	...	8.4-9.3
2.4	...	...	(148-) 175.6-183.1	...	...
...	...	...	134.1-191.7	...	...
0.2	4.75	1.15	(123-) 138.8-177	204	165-170
...	...	...	(91-94-) 125-146	...	...
Reichert value, 3.7-12.5	...	...	(81-) 106-131	...	130-132
22-24	...	...	126.9	...	...
Reichert value, 5.6-66	...	...	33-99	...	...
Reichert value, 1.3	7.1	5.4	78.7-84	...	...
...	6.7	5.4	80.4-82.1	...	...
...	4.6	2.6	4	...	...
...	17.4	15.2	8.8-10.7	...	...
...	57.5	55.2	13.5	...	...
...	32.6	23.3	(10-) 20-21 (-28)	...	...

‡ Iodine value. Low results were obtained in the older determinations owing to the use of an insufficient excess of the reagent. Low results in the case of the drying oils may also be due to the sample having undergone oxidation. Thus the lower figures given in the table represent values which may not now be expected.

THE PHYSICAL PROPERTIES OF THE OILS, FATS, AND WAXES

The Insoluble Fatty Acids.								
		Specific Gravity.	Refractive Index.	Melting Point.	Solidifying Point.	Specific Gravity.	Melting Point.	Solidifying Point.
Drying oils—				° C.	° C.		° C.	° C.
Linseed	.	$\frac{15.5}{15.5}$ 0.930-0.937 $\frac{99}{15}$ 0.8809	{ 15° C., 1.481 60° C., 1.4674	- 16 to - 20	16, - 27	$\frac{15.5}{15.5}$ 0.923, $\frac{100}{100}$ 0.8925	17-24	13-17
Hemp-seed oil	.	$\frac{15}{15}$ 0.925-0.933	—	...	- 27.5	...	17-19	16
Wood oil	.	$\frac{15.5}{15.5}$ 0.934-0.943	...	...	Below - 17(?)	...	30-49	17-34
Candle-nut oil	.	$\frac{15.5}{15.5}$ 0.9256	15° C., 1.4756-1.4759	...	...	...	20-21	13
Walnut oil	.	$\frac{15.5}{15.5}$ 0.921-0.926	40° C., 1.4689-1.4710	...	...	...	16-20	14-3
Poppy-seed oil	.	$\frac{15.5}{15.5}$ 0.923-0.9268 (0.937)	40° C., 1.4680	...	- 18	...	20-21	16-19
Niger-seed oil	.	$\frac{15.5}{15.5}$ 0.9248-0.9270	40° C., 1.4678	...	Below - 9	...	...	...
Semi-drying oils—								
Sunflower-seed oil	.	$\frac{15}{15}$ 0.924-0.926	...	...	...	...	22-24	17-19.8
Maize oil	.	$\frac{15.5}{15.5}$ 0.924-0.928	{ 15° C., 1.4765-1.4767 60° C., 1.4605	...	- 36	100° C., 0.8529	17-22.4	...
Pumpkin-seed oil	.	$\frac{15}{15}$ 0.917-0.925	25° C., 1.4723-1.4738	...	- 15	...	26.5-28.5	...
Sesamé oil	.	$\frac{15}{15}$ 0.921-0.926	{ 15° C., 1.4746 60° C., 1.4580	...	...	...	24.2-31	18-28
Cotton-seed oil	.	$\frac{15.5}{15.5}$ 0.920-0.928 ( $\frac{15}{15}$ 0.930)	{ 15° C., 1.475 60° C., 1.4586	...	...	$\frac{100}{100}$ 0.8816	35-40	32-38
Rape-seed oil	.	$\frac{15.5}{15.5}$ 0.912-0.917	{ 15° C., 1.4745 60° C., 1.4584	...	- 1 to - 10	$\frac{100}{100}$ 0.8758	17-21	12-16.5
Black mustard oil	.	$\frac{15.5}{15.5}$ 0.915-0.919	40° C., 1.4655	...	- 17.5	...	16-17	15
White mustard oil	.	$\frac{15.5}{15.5}$ 0.912-0.915	40° C., 1.4649	...	- 8 to - 16	...	15-16	...



Non-drying oils and solid fats—

Earth-nut oil . . . . .	$\frac{15.5}{15.5}$ 0.916-0.9256	...	-3 to -7	{ 15° C., 1.4731 60° C., 1.4564	$\frac{100}{100}$ 0.8475-0.864	27-32	22-30
Almond oil . . . . .	$\frac{15.5}{15.5}$ 0.917-0.9195	...	-10 to -21	{ 25° C., 1.468-1.467 60° C., 1.4555	...	14	5-14
Croton oil . . . . .	$\frac{15.5}{15.5}$ 0.940-0.960; 100° C., 0.8874	...	-16	27° C., 1.4768	...	...	16.4-19
Grape-seed oil . . . . .	15° C., 0.920-0.596	..	-10 to -17	...	...	23-25	18-20
Castor oil . . . . .	$\frac{15.5}{15.5}$ 0.960-0.967	...	-10 to -18	{ 15° C., 1.4803 60° C., 1.4647	...	13	3
Olive-kernel oil . . . . .	$\frac{15.5}{15.5}$ 0.918-0.920	...	...	1.4682-1.4688	...	...	...
Olive oil . . . . .	$\left(\frac{15}{15}\right)$ 0.914 15.5 0.917-0.920 15.5 $\frac{100}{100}$ 0.862-0.864	...	...	{ 15° C., 1.4718 60° C., 1.4546	{ $\frac{60}{15}$ 0.878 $\frac{100}{100}$ 0.8749	22-26	21-24
Ben oil . . . . .	$\frac{15}{15}$ 0.9120	...	...	...	...	...	...
Neat's foot oil . . . . .	$\frac{15}{15}$ 0.914-0.919 $\frac{15}{15}$ 0.931-0.938	...	...	{ 15° C., 1.473 60° C., 1.4559	$\frac{100}{100}$ 0.8742-0.8800	28-30	16-26.5
Lard . . . . .	$\frac{60}{15.5}$ 0.886 $\frac{100}{15}$ 0.860-0.862	40-45	27-30	{ 40° C., 1.458-1.460 60° C., 1.452	—	35-45	37-39
Lard oil . . . . .	$\frac{15.5}{15.5}$ 0.917 $\frac{100}{100}$ 0.8626	...	...	...	0.885	35	31
Mahwa butter ( <i>Bassia latifolia</i> ) - Mowrah seed oil ( <i>Bassia longifolia</i> )	$\frac{100}{100}$ 0.8943-0.8975 100° C., 0.8854	23.0-31.0 35.5-42	19-22 25-36	40° C., 1.4605-1.4609 ...	...	45 54.5-55.5	40 52.5
Palm oil . . . . .	$\frac{60}{15.5}$ 0.8837 $\frac{100}{100}$ 0.858	...	...	60° C., 1.451	$\frac{100}{100}$ 0.870	47-50	40-45
B one fat . . . . .	$\frac{15.5}{15.5}$ 0.914-0.916 $\frac{60}{15.5}$ 0.894	21-22	...	60° C., 1.451	...	30-42	28-32

THE PHYSICAL PROPERTIES OF THE OILS, FATS, AND WAXES (continued)

The Insoluble Fatty Acids							
	Specific Gravity.	Melting Point.	Solidifying Point.	Refractive Index.	Specific Gravity.	Melting Point.	Solidifying Point.
Non-drying oils and solid fats (cont.)							
Tallow (beef)	$\frac{60}{15.5}$ 0.901, $\frac{100}{100}$ 0.860	42-48	° C.	{ 40° C., 1.4987 60° C., 1.442	...	° C.	° C.
Tallow (mutton)	$\frac{60}{15.5}$ 0.907	47-51	...	60° C., 1.4531	...	45-50	42.5-45
Tallow oil	$\frac{100}{100}$ 0.794	...	...	...	...	...	43-46
Cocoa (cacao) butter	$\frac{100}{100}$ 0.903-0.904	23-5-33	...	{ 40° C., 1.448-1.458 60° C., 1.450-1.458	...	45-51	35-37.5
Vegetable tallow	...	37-46	24-31	...	...	40-57	47.2-49.2
Butter fat	$\frac{40}{15.5}$ 0.904-0.9102 $\frac{100}{15}$ 0.865-0.870 $\frac{100}{100}$ 0.909-0.914	29-34.6	19-20	{ 25° C., 1.459-1.462 60° C., 1.445-1.450	$\frac{20}{20}$ 0.9106-0.9242	38-43	34-48
Palm-kernel oil	$\frac{60}{15.5}$ 0.896, $\frac{99}{15}$ 0.873	23-28	...	{ 40° C., 1.450 60° C., 1.443	...	21-28	...
Japan wax	$\frac{60}{15.5}$ 0.902-0.907 $\frac{98}{15.5}$ 0.875	42-45	...	60° C., 1.450	...	56-57	53-56.5
Myrtle wax	$\frac{98}{15.5}$ 0.875	40-44	39-5-43	...	$\frac{99}{15.5}$ 0.837	47-5	46.0
Cocoa-nut oil	$\frac{60}{15.5}$ 0.897, $\frac{99}{15.5}$ 0.874	...	...	{ 40° C., 1.445-1.450 60° C., 1.442	...	24-27	19-23
Marine animal oils—							
Menhaden oil	$\frac{15.5}{15.5}$ 0.932-0.935 $\frac{15}{15}$ 0.925-0.928	...	-4	...	...	...	...
Sardine oil	$\left(\frac{15}{15}\right)$ 0.916-0.933	20-22	...	15° C., 1.479	...	30-31	...
Cod-liver oil	$\frac{15.5}{15.5}$ 0.922-0.935	...	...	{ 15° C., 1.482 60° C., 1.462-1.466	$\frac{60}{60}$ 0.882	21-25	...





as well as the potassium salts of several fatty acids.—Sp. gr. 0.943 (17° C.), 0.90 at 100° C.; sol. pt. 30°; M.P. 36°–42° C.; refract. index (60° C.) 1.465; sap. val. 80–100; iod. val. 20–29; fatty acids, 60 per cent.; alcohols, 43–50 per cent. Mixed fatty acids melt 41° C.; iod. val. 17; mol. wt. 327. Mixed alcohols, M.P. 33° C.; iod. val. 26–36; acetyl. val. 144; mol. wt. 239.

**Pure Lanolin** is perfectly neutral, does not become rancid, and is very difficult to saponify; its capacity for absorbing water is most remarkable, taking up when kneaded 110 per cent. to form a cream; it similarly takes up glycerin. The skin absorbs it in an extraordinary way, and thus it serves as an excellent basis for introducing effective remedies through the skin; for instance a lanolin corrosive sublime ointment containing but  $\frac{1}{1000}$  per cent. of corrosive sublimate produces a metallic taste upon the tongue within a few minutes of application to any part of the body! Lanolin consequently forms an excellent basis—either hydrated or combined with glycerin—for ointments, pomatums, and cosmetics.

### Distilled Grease

Yorkshire grease from wool and soap suds is often too dirty and odoriferous to be used for anything except cart grease and rough lubricating materials for rollers, etc. To obtain a better product it is often distilled in cast-iron stills holding about 4 tons of grease, first for ten to sixteen hours over a free fire (to remove water), and then for twenty to twenty-four hours with superheated steam.

“**Spirit Oil**” (*sometimes, not always*) comes over first. Pale yellow oil, darkens on keeping, boils over at 150°–320° C. Used in making black varnish.

**First Distilled Grease** is the second product coming over. It is often allowed to crystallise, and is then pressed for liquid **oleic acid** and solid “**stearine**” (M.P. 48°–57° C.). It is sometimes redistilled (“**second distilled grease**”).

The next product to distil is the “**green oils**,” sometimes used for coarse lubricating greases; more often mixed with another batch of material and redistilled.

**Pitch** remains behind in the still. It is used as a lubricant for the necks of hot rollers.

Wright gives the following numbers for the distillation of 100 parts Yorkshire grease:—Pitch, 14 per cent.; green oil, 15.5 per cent.; first distilled grease, 45.5 per cent.; spirit oil, 4 per cent.; water and loss, 21 per cent. Lewkowitsch finds in distilled grease 55 per cent. free fatty acids; 7 per cent. combined fatty acids; 39 per cent. unsaponifiable matters.

### Solid Vegetable Waxes.

**Carnaüba Wax** is exuded by the leaves of the Brazilian wax palm, *Coryptia cerifera*, and consists principally of myricyl cerotate. Used in candle manufacture, polishing pastes (wax varnishes), and in making gramophone records.—M.P. 84° C.; acid val. 4–8; sap. val. 79–95; iod. val. 13. True acetyl. val. 55; sp. gr. (15° C.), 0.99–1.0, 0.84 at 100°.

Other vegetable waxes are flax wax, gondang wax, pisum wax, opium wax, palm wax, ocuba wax, cotton-seed wax.

**Candelilla Wax** occurs on the stems of *Pedilanthus pavonis*, a Mexican plant, and consists of  $C_{29}H_{60}$ ,  $C_{31}H_{64}$ , and  $C_{33}H_{68}$ , together with esters. It is extracted by immersing the plants in boiling water. The wax is brown in colour and of a brittle nature. It may be bleached, as may Carnaüba wax, and is employed industrially in a similar way.

**Flax and Cotton-seed Waxes** occur in the seed fibres of flax (2 per cent.) and cotton (1 per cent.).

**Montan Wax** occurs in lignite and peat. It is extracted with benzine. The composition of Montan wax is variable, but always contains esters of montanic acid,  $C_{30}H_{56}O_2$ , together with the free acid and hydrocarbons. Very high melting-point alcohols are also present.



## IV.—METHODS OF EXAMINATION OF FATTY OILS

By the late AINSWORTH MITCHELL, B.A., F.R.I.C.

### LITERATURE

See under Animal and Vegetable Fatty Oils; also HILDITCH, "Industrial Fats and Waxes," Baillière, Tindall & Cox.

**Methods of Examination.**—Only in exceptional cases (such as sesamé oil and cotton-seed oil, which contain characteristic compounds) is it possible to directly identify a given fatty oil by means of a reagent, and it is therefore necessary to apply physical and chemical tests, which will locate the oil in successively narrowing groups and finally to apply similar tests of identity.

The methods employed include a determination of the so-called "constants" or values of the sample, such as the specific gravity, solidification and melting points, optical properties, amount of iodine absorbed (iodine value), amount of alkali required for saponification (saponification value), amount of volatile and insoluble fatty acids present in the oil (Reichert and Hehner values), etc.

The difficulty of the task is often increased by the fact that oils and fats of the same kind show considerable variations in their constants—so much so that an oil—*e.g.*, olive oil—may contain a considerable proportion of an adulterant such as maize oil, and still show values falling within the higher limits recorded for the pure natural oil. This will be seen more clearly in the following details concerning the "values."

**Specific Gravity.**—This is usually determined at a temperature of  $15.5^{\circ}$  C. in the case of oils and at  $100^{\circ}$  C. in the case of solid fats, water at  $15.5^{\circ}$  C. being taken as unity. *Tables of Specific Gravities* are given, pp. 56-59.

The following table, based on a system first proposed by Allen, illustrates the assistance given by the specific gravity in the classification of oil.

### OILS.

Sp. gr. 0.913-0.920 ( $15.5^{\circ}$ C.).	Sp. gr. 0.920-0.925 ( $15^{\circ}$ C.).	Sp. gr. 0.925-0.935	Sp. gr. 0.935-0.960 ( $15.5^{\circ}$ C.).
Almond oil. Colza    " Arachis  " Olive     "	Cotton-seed oil. Maize     " Sesamé    " " Cod-	Linseed oil. Whale    " " " Liver oil.	Tung oil. Castor    " Croton    " "

### FATS AND WAXES.

Sp. gr. 0.800-0.855 ( $100^{\circ}$ C.).	Sp. gr. 0.855-0.863 ( $100^{\circ}$ C.).	Sp. gr. 0.863-0.867 ( $100^{\circ}$ C.).
Spermaceti. Bee wax. ... ...	Palm oil. Cacao butter. Tallow. Lard.	Cocoa-nut oil. Japan wax. Butter fat. ...

**Refractive Index.**—Oils frequently show pronounced differences in their refractive index—so much so that this value when determined by means of a refractometer at a definite temperature may afford decisive proof of adulteration. Thus in the case of butter fat Wollny obtained readings varying from 1.4560-1.4620, while margarine gave readings of 1.4650-1.4700, and mixtures of butter and margarine readings of 1.4620-1.4690.

A special instrument termed a "butyro-refractometer," in which the readings are given in degrees on a scale, is widely employed for this purpose, and is particularly useful as a sorting test. As is evident, however, from the examples quoted above, a mixture of butter with a small percentage of margarine may give refractometer readings falling within the limits of those of genuine butter. (See *Tables*, pp. 56-59.)

**Melting and Solidification Points.**—The temperatures at which fats or oils melt or solidify also afford means of identifying different samples. For instance, almond oil does not solidify until chilled to  $-20^{\circ}$  C., whereas olive oil solidifies at about  $2^{\circ}$ - $4^{\circ}$  C. These differences largely depend upon the nature of the fatty acids in the glycerides. Thus olive oil contains a large proportion of the glycerides of solid fatty acids, whilst in almond oil such glycerides are only present in traces, the oil consists chiefly of glycerides of liquid fatty acids. (See *Tables*, pp. 56-59.)

The melting points of the separated fatty acids may also afford valuable information. The following are a few solidifying points of fatty acids obtained from various oils and fats (the numbers represent Centigrade degrees):—

Beef tallow, 38-46.	Tung oil, 37.
Mutton tallow, 41-48.	Hemp oil, 14-16.
Lard, 34-42.	Poppy-seed, 16.5
Horse fat, 33.7.	Cotton-seed, 32-36.
Neat's foot oil, 26.5.	Rape, 12-18.
Palm oil, 36-45.	Olive, 17-26.
Cocoa-nut oil, 20-25.	Arachis, 23-29.
Palm-nut oil, 20-25.	Cod-liver, 18-24.
Japan wax, 59.	Whale, 24.
Vegetable tallow, 45-53.	Japanese sardine, 28.
Linseed oil, 13-17.	

**The Acid Value.**—This is a measure of the quantity of potassium hydroxide required to neutralise the free fatty acids in an oil. Gradual decomposition of the glycerides into their components glycerol and free fatty acids takes place when a fat is exposed to the action of light and air, with the result that the acid value steadily rises. This value may therefore be a test of the freshness of an oil. Old and rancid fats sometimes have very high acid values. (See *Table*, p. 54.)

**Saponification Value.**—The oil is boiled with a measured excess of alkali in suitable solution, and the amount (expressed in milligrammes of potassium hydroxide) required to effect complete decomposition of one gramme of the fat into soap and glycerol or other alcohol is termed the saponification value.

As the fatty acids possess different molecular weights, the proportion of alkali required to neutralise them will also vary, and the oils containing them will have different saponification values. (See *Tables*, pp. 54, 55.)

By way of example, the following saponification values may be quoted:—

Castor oil, 176-183.	Cocoa-nut oil, 255-260.
Cod-liver oil, 182-187.	Beeswax, 90.
Cotton-seed oil, 192-193.	Paraffin wax, 0.
Olive oil, 190-195.	Wool wax, 102.
Linseed oil, 190-195.	Insect wax, 90.
Almond oil, 190-192.	Spermaceti, 123-134.
Lard, 195-196.	Sperm oils, 123-136.
Butter fat, 225-230.	



Hence, if a sample of lard showed a saponification value of, say, 200, the presence of cocoa-nut oil would be suggested and further tests for that fat would be applied.

NOTE.—(1) Waxes, both liquid and solid, are characterised by such low saponification values that they are easily distinguished by this means from oils.

(2) The majority of oils and fats have saponification values about 193. Higher or lower values than this may suggest the presence of special oils.

(3) Mineral oils have a zero saponification value, and consequently their presence lowers the saponification value of a fatty oil.

**Iodine Value.**—The liquid fatty acids, which form the principal constituent of the glycerides in fluid oils, are unsaturated compounds, and will combine with bromine or iodine (in suitable form) to form saturated bodies. The percentage of iodine absorbed in this test is termed the iodine value, and is a most valuable means of identifying different groups of oil.

One class of oils, typified by almond and olive oils, consists largely of oleic acid (which absorbs approximately 90 per cent. of iodine). These have iodine values of about 80-95, and are known as **non-drying oils**.

Another group contains oils in which linolic acid (absorbing about 181 per cent. of iodine) is an important constituent. Cotton-seed oil (iodine value, about 108), sesamé oil (iodine value, 110), and maize oil (iodine value 120) are examples of these oils, which are termed **semi-drying oils**.

A third important group contains the **drying oils**, in which the glyceride of linolenic acid (iodine value, 274) is usually an important constituent. They naturally have high iodine values, *e.g.*, linseed oil, 195; nut oil, 142.

Marine animal oils also have high iodine values, due to the presence of highly unsaturated fatty acids, but they may be distinguished from drying oils by their non-drying properties, and by other tests.

Solid fats have iodine values which are greater in proportion to the amount of unsaturated fatty acids they contain. Lard, for instance, usually has an iodine value of 50-60, so that a high iodine value (*e.g.*, 70) points to the lard having been stiffened with beef fat, and then rendered sufficiently fluid again by the addition of a vegetable oil, such as maize or cotton-seed oils.

Certain kinds of American lard, however, normally have high iodine value (up to 66), and it is therefore necessary to confirm the presence of a vegetable oil in lard by other tests (see p. 66).

#### IODINE VALUES OF COMMON OILS, FATS, AND WAXES (see p. 55)

Oleic acid, 90.	Sunflower oil, 118-136.
Tallow, 35-46.	Hemp-seed oil, 140-166.
Butter, 36-48.	Poppy-seed oil, 137-143.
Lard, 50-65.	Walnut oil, 143-148.
Mutton fat oil, 32-57.	Seal oil, 127-146.
Oleo-margarine, 53-88.	Whale oil, 121-146.
Olive oil, 79-93.	Cod-liver oil, 154-181.
Sesamé oil, 103-112.	Shark liver, 115.
Rape oil, 94-108.	Menhaden oil, 175-183.
Cotton-seed oil, 105.	Sardine oil, 161-193.
Castor oil, 83-86.	Porpoise oil, 131.
Arachis oil, 90-103.	Sperm oil, 81-84.
Palm oil, 51-57.	Arctic sperm oil, 67-82.
Cocoa-nut oil, 8-9.	Insect wax, 1.4.
Palm-kernel oil, 10-17.	Beeswax, 10.
Croton oil, 101-109.	Spermaceti, 4.
Linseed oil, 179-200.	Wool wax, 17.
Tung oil, 149-167.	Carnaüba wax, 13.

NOTES.—(1) Linseed oil has a high iodine value, and adulteration with foreign oils lowers that value.

(2) The addition to walnut or poppy-seed oil of 5-10 per cent. of rape or cotton-seed oils and 20 per cent. linseed has an influence on the iodine value.

(3) The adulteration of olive oil with only 5 per cent. of a drying oil and 15 per cent. of cotton seed, sesamé, rape, or arachis oil may be suggested by the iodine value.

(4) Fish oils have very high iodine values, and their presence is thus indicated in oils with low iodine values but not in drying oils.

(5) If  $I$  denotes the iodine value of a mixture of two fats whose iodine values are  $m$  and  $n$  respectively, then, percentage of fat  $m = \frac{100(I - n)}{m - n}$ .

**Hehner Value.**—This test devised by Hehner indicates the percentage of insoluble fatty acids which can be separated from an oil or fat. It is usually about 93-96, but in the case of fats (such as butter, cocoa-nut oil, and palm oil) which contain a high proportion of volatile and soluble fatty acids it is much lower. Thus butter usually has a Hehner value ranging from 85-88, and cocoa-nut oil a value of 88-90.

We give a few numbers; for others see *Table*, p. 54:—

100 g. cow's butter fat contain 86-89 g. insoluble fatty acids.

" tallow	" 96	" "
" lard	" 96	" "
" olive oil	" 95	" "
" poppy seed	" 95	" "
" palm oil	" 96	" "
" palm kernel	" 91	" "
" cocoa-nut oil	" 89	" "
" dolphin jaw oil	" 66	" "
" porpoise jaw oil	" 70	" "

**Reichert Value.**—This is a measure of the amount of alkali expressed in c.c. of decinormal solution, required to neutralise the proportion of volatile soluble fatty acids liberated and distilled under the constant conditions laid down by Reichert. A modification of the method devised by Meissl is more commonly employed, the value being termed the **Reichert-Meissl** value, and relating to 5 g. instead of 2.5 g. of the fat. The following are a few typical Reichert-Meissl values (for others see *Table*, p. 56):—

Butter fat, 28 c.c. (24-33).	Cocoa-nut oil, 7-8 c.c.
Beef tallow, 0.5 c.c.	Maize oil, 0.3-4.4 c.c. (Reichert).
Olive oil, 0.6 c.c.	Croton oil, 13 c.c.
Sesamé oil, 0.7 c.c.	Dolphin oil, 11 c.c.
Rape oil, 1.0 c.c.	Dolphin jaw oil, 130 c.c.
Palm oil, 1.0 c.c.	Porpoise body oil, 46 c.c.
Palm-kernel oil, 5 c.c.	Porpoise jaw oil, 100-139 c.c.

Most of the solid animal body fats have only trifling Reichert-Meissl values, but in butter fats the proportion of volatile fatty acids is high, and correspondingly high values are obtained in the test.

Thus in the case of cow's butter the value normally ranges from about 24 to about 33. Hence when a sample of butter shows a Reichert value of, say, 20, the addition of an adulterant is probable. In the case of certain kinds of Dutch cows, however, the butter fats sometimes give a value as low as 17, this being attributed to leaving the herds in the fields too late in the season.

Most vegetable oils and fats have a Reichert-Meissl value of less than 2, but cocoa-nut oil has a value of 7-8, and palm-kernel oil a value of about 4. A considerable amount of these fats may, therefore, be added to butter without rendering the Reichert value suspiciously low.

Of late several methods of detecting these fats in butter have been based upon a separation of the fatty acids intermediate between the quite insoluble acids and those readily volatile. Cocoa-nut oil and palm-kernel oil are particularly rich in these acids, and therefore show an "extended" Reichert value, which is not given by butter. (See also pp. 75, 87.)



**Maumené Test.**—Weigh 50 g. of oil into a 200 c.c. tall beaker packed with cotton wool into a litre beaker; run in slowly (take sixty seconds) from a burette 10 c.c. of concentrated sulphuric acid, stirring continually with a thermometer; the highest temperature attained is the required value.

Olive oil, 42° C.  
Almond oil, 52°-54° C.  
Rape oil, 57°-60° C.  
Arachis oil, 45°-75° C.  
Sesamé oil, 68° C.  
Cotton seed, 75°-90° C.  
Poppy seed, 88° C.  
Walnut, 101° C.  
Hemp seed, 98° C.  
Linseed, 103°-145° C.  
Castor, 47° C.

Tallow oil, 41°-44° C.  
Neat's foot, 48° C.  
Cod liver, 102°-103° C.  
Skate liver, 102° C.  
Menhaden, 126° C.  
Seal, 93° C.  
Whale, 92° C.  
Porpoise (body), 51° C.  
Sperm, 51° C.  
Arctic sperm, 41°-47° C.

Drying oils have a high Maumené value; so also have fish oils. Non-drying oils have a low value.

**Elaidin Test.**—Useful for detecting drying oils mixed with non-drying, and *vice versa*. Measure 50 c.c. of oil into a wide-mouthed stoppered bottle of 100 c.c. capacity; add 2 c.c. of cold, freshly-made mercury nitrate (prepared by dissolving 13 g. mercury in 12 c.c. concentrated nitric acid, keeping cold in cold water to retain nitrous fumes), shake well; place in air oven at 25° C. for twenty-four hours, agitating from time to time; simultaneously perform a comparison experiment with a standard sample of oil, and compare results. Note length of time of solidification and consistency of mass after twenty-four hours.

**Drying Oils** (linseed, hemp seed, walnut, poppy, etc.) remain *fluid*.

**Semi-drying Oils** (rape, neat's foot, sperm, cotton seed, etc.) yield after twenty-four hours a thick mass of treacle-like consistency.

**Non-drying Oils** (olive, sperm, tallow, etc.) turn into a solid mass.

The following examples show the use of these constants in analytical work.

1. A sample of oil sold as olive oil had the following characteristics: Sp. gr. 0.924; acid value, 4; saponification value, 190; iodine value, 105; refractometer reading, 67; melting point of fatty acids, 24° C.

The iodine value at once indicated that this was not pure olive oil, and the other values agreed with those of pure sesamé oil. This was confirmed by a special colour reaction for that oil, and by the fact that it slowly dried on exposure in a thin film to the air.

2. A solid fat sold as lard gave the following results: Iodine value, 72; and Reichert-Meissl value, 2.5. The high iodine value suggested the presence of a vegetable oil, and this was found by special colour reactions to be cotton-seed oil. The Reichert-Meissl value indicated the presence of cocoa-nut oil, and this was confirmed by other tests.

**Differentiation of Fish Oils from Drying Oils.**—Oils such as cod-liver oil (and marine animal oil, whale, etc.) may be distinguished from linseed and other drying oils by drying tests, and by the fact that on treatment with bromine they yield an insoluble white compound, which turns black when heated.

The corresponding compound from linseed oil treated in the same way melts to form a colourless liquid. The following list gives the percentage yield of insoluble bromides from certain typical oils: \*—

Linseed, 24-38.  
Tung oil, *nil*.  
Candle-nut oil, 8.  
Walnut oil, 1.4-1.9.  
Poppy-seed oil, *nil*.  
Maize oil, *nil*.  
Cotton-seed oil, *nil*.  
Brazil-nut oil, *nil*.  
Olive oil, *nil*.

Almond oil, *nil*.  
Fish oil (deodorised), 50.  
Cod-liver oil, 30-43.  
Japan fish oil, 22.  
Shark liver, 20.  
Seal oil, 28.  
Whale oil, 15-26.  
Sperm oil, 2.4-3.7.

**Mineral Oils in Fatty Oils.**—In order to detect mineral oils, paraffin wax, and other unsaponifiable matters in fats, we proceed thus: Saponify with alcoholic potash, evaporate to dryness on

\* This test was originated by C. A. Mitchell. Lewkowitsch and others invariably describe these insoluble bromides as "hexabromides." They are the bromides of mixed glycerides and certainly not hexabromides.



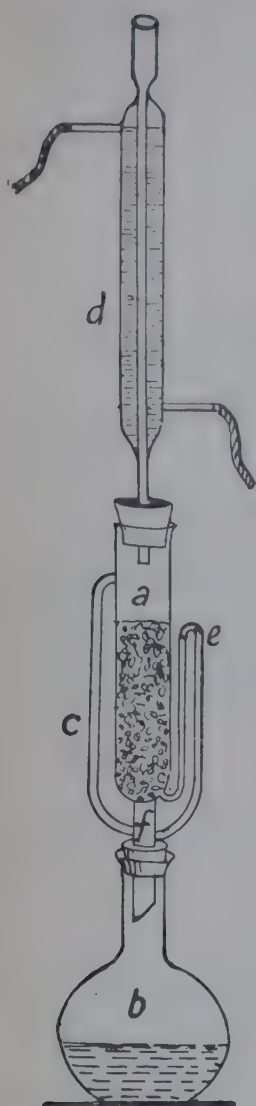


FIG. 20.—Soxhlet Fat Extraction Apparatus.

the water bath, extract the unsaponifiable matter with petroleum spirit or ether, evaporate the solvent, and the residue represents the amount of unsaponifiable matter. The saponification is effected thus: Weigh out 10 g. fat into a porcelain basin, add 50 c.c. of 8 per cent. alcoholic potash solution, boil on water bath until soap begins to froth, then add 15 c.c. alcohol and boil until the soap is dissolved. Stir into the mass 5 g. sod. bicarbonate and 50-60 g. recently ignited pure white sand; dry twenty minutes in water oven, transfer to a Soxhlet apparatus, extract with petroleum spirit (B. P. below 80° C.), distil off petroleum spirit and weigh residue. **Waxes** require prolonged boiling for complete saponification, but are more easily saponified if boiled with a freshly-made solution of sodium (5 g.) in absolute alcohol (100 c.c.). The Soxhlet apparatus used for extraction is shown in the figure. The substance to be extracted is placed in the tube *a*, which is closed at *f*. In *b* petroleum spirit is placed and heated to boiling point. The vapour rises through *c* into the condenser *d*, and, descending in the form of drops, gradually fills *a* with liquid to the level of the bend in the tube *e*; when this happens, the liquid syphons over into the flask *b*, bearing with it the extracted matter. Then the process begins anew, a continual stream of solvent flowing through *a* until all the extractable matter is removed from the substance. The fluid in *b* is then distilled, and the extracted matter remaining behind is dried at 100° and weighed.

### To Distinguish Between Animal and Vegetable Oils and Fats

**Animal Oils** and fats contain the alcohol **cholesterol**,  $C_{27}H_{46}O$ . **Vegetable fats** contain a similar alcohol called **phytosterol**,  $C_{27}H_{46}O$ . This fact allows us to distinguish between animal and vegetable fats. If the fat contains both cholesterol and phytosterol it is a mixture of animal and vegetable fats. The method of examination is as follows: Saponify a considerable quantity of fat by alcoholic potash; the cholesterol or phytosterol remains in the unsaponifiable matter. If the body is a wax, saponify with sodium dissolved in absolute alcohol.

1. Dissolve the unsaponifiable matter in ether, filter if necessary, evaporate off the ether, redissolve in absolute alcohol, and allow to crystallise on a watch glass; examine crystals under the microscope. Crystals of cholesterol have a different shape from those of phytosterol.

2. Heat crystals obtained in 1 with 2-3 c.c. of acetic anhydride in a small dish covered with a watch glass; evaporate off the acetic anhydride on the water bath and crystallise twice from alcohol. Take melting point in the usual way.

**Cholesteryl acetate** melts 114°-115°; **Phytosteryl acetate** melts 125°-137° C. Hence they are easily distinguished.

If both cholesteryl and phytosteryl acetates are present fractionally crystallise the mixture several times from alcohol and thus separate the crystals into high melting and low melting portions, and examine these separately.

In recent years many of the analytical methods have been scrutinised by committees set up by various scientific societies, and there has come into existence a large number of reports by these committees on one or other of these methods, *e.g.*, in the *Analyst* and the *American Oil and Fat Industries*.

### Recommended Methods for the Testing of Fats

#### 1. Saponification Value.

(a) Weigh accurately about 5 gm. of the material into a 300 c.c. flask, and mix with 30 c.c. of neutral alcohol.

(b) Run in 50 c.c. of N/2 alcoholic potash, with constant stirring, taking the same time with each repetition, *e.g.*, 2 minutes.

(c) Boil the contents of the flask for 1 hour under reflux, with occasional shaking.

(d) Carry out a blank experiment at the same time.

(e) Add 1 c.c. of phenolphthalein solution to each flask, and both titrated with standard acid, *e.g.*, N acid.

Then let *W* be the weight of fat taken and  $V_w$  and  $V_b$  the volumes of normal acid required to neutralise the saponified solution and the blank respectively after refluxing. We have

$$\text{saponification value} = \frac{(V_b - V_w) \times 56.1}{W}$$

and

$$\text{saponification equivalent} = \frac{1000W}{V_b - V_w}$$



## 2. Free Fatty Acids.

When these are large in quantity an estimate may be obtained by noting the titration value of the alcoholic potash when adding this to the alcoholic solution of the fat (warm). (See last section on Saponification Value.) The rest of the alcoholic potash is then, of course, added and the saponification completed. When, however, the free fatty acid is small the following method is recommended:

- (a) Weigh out 10 gm. of sample into a 250 c.c. flask.
- (b) Add 25 c.c. alcohol (neutral) and 50 c.c. light petroleum.
- (c) Boil solution for 2 minutes.
- (d) Add a few drops of phenolphthalein solution.
- (e) Titrate with vigorous shaking against a solution of N/10 alcoholic potash until a pink colour appears and remains fairly permanent.

Then if  $V$  c.c. of  $N$  alkali are required to neutralise  $W$  gms. of material,

$$\text{acid value} = \frac{V \times 56.1}{W}$$

and

$$\text{percentage fatty acid} = \frac{V \times 28.2}{W} \text{ (as oleic acid).}$$

## 3. Iodine and Thiocyanogen Absorption.

IODINE VALUE (see p. 63).

(a) Prepare Wijs solution by dissolving 8.5 gm. iodine and 7.8 gm. iodine monochloride in warm glacial acetic acid, and making up to 1,000 c.c. with cold glacial acetic acid, and

- (b) Prepare standard (N/10) sodium thiosulphate.
- (c) Prepare a 10 per cent. potassium iodide solution and a starch solution.
- (d) Pure, dry chloroform or carbon tetrachloride is required.
- (e) Weigh out 0.1–0.5 gm. of the fat (depending on the suspected degree of unsaturation) into a wide-mouthed bottle fitted with a ground-glass stopper.
- (f) Dissolve in 15 c.c. of pure chloroform or carbon tetrachloride.
- (g) Add 25 c.c. of Wijs solution and shake well, leaving in the dark for one hour. (10 c.c. of 2½ per cent. of mercuric acetate is said to shorten this time to 3 minutes.)

(h) When contact time is complete, the solution is mixed with 15 c.c. of 10 per cent. potassium iodide solution and titrated with standard sodium thiosulphate solution, using starch.

(i) Carry out a blank experiment concurrently without the fat. Then if  $W$  is the wt. of the fat and  $V_w$  and  $V_b$  are the volumes of  $\frac{N}{10}$  thiosulphate required in the actual and blank experiment respectively, then

$$\text{iodine absorption} = \frac{(V_b - V_w) \times 1.27}{W} \text{ per cent.}$$

**Thiocyanogen Absorption** (Haufmann, 1925).—This test is intended to discriminate between oleic, linoleic and linolenic acids. Thiocyanogen reacts with approximately one out of two double bonds in linoleic compounds, a little less than two out of three double bonds in linolein compounds.

(a) Prepare the thiocyanogen reagent by drying lead thiocyanate thoroughly over phosphorus pentoxide in a vacuum (about one week is required).

(b) Meanwhile glacial acetic acid is refluxed with 15 per cent. acetic anhydride for 3 hours and then allowed to stand for 3 days.

(c) 50 gm. of the dried lead thiocyanate is suspended in 1,000 c.c. of the prepared acetic acid, well shaken, and left in the dark for a week in a well-stoppered bottle.

(d) Dry all filter paper before use at 120° C.

(e) Add to the prepared lead thiocyanate in acetic acid exactly enough bromine to liberate thiocyanogen and convert all the lead into lead bromide. The strength of the reagent should be 0.16–0.20 N. Each batch must be filtered to a clear solution.

(f) Weigh out 0.2 gm. of the fat and dissolve in 20 c.c. of the prepared acetic acid.

(g) Place in contact with 20 c.c. of the filtered reagent for 24 hours at 20° C. (approx.) in the dark.

(h) Add 20 c.c. of 20 per cent. aqueous potassium iodide solution.

(i) Titrate with standard thiosulphate.

The method is uncertain unless timing of the reactions is accurate for the fats being composed, and water must be rigidly excluded until (h) above.

#### 4. Reichert-Meissl Value (see p. 64).

(a) Saponify exactly 5 gm. of the fat in a 300 c.c. flask by means of 2 c.c. of 50 per cent. caustic soda and 10 c.c. of 92 per cent. alcohol for 15 minutes.

(b) Evaporate off the alcohol and dissolve the dry soap in 100 c.c. distilled water, acidifying with 50 c.c. N sulphuric acid.

(c) Distil the aqueous mixture, collecting as closely as possible 110 c.c. of distillate in half an hour. It is recommended that the apparatus should be that laid down by Polenske.

(d) Filter the distillate and titrate 100 c.c. of it against N/10 caustic soda with phenolphthalein as indicator.

The Reichert-Meissl value is then  $1.1 \times \text{vol. of alkali required}$ .

#### 5. Acetyl Value.

This is the number of milligrams of potassium hydroxide required to neutralise the acetic acid produced by hydrolysis of one gram of an acetylated fat. It is a guide to the number of free hydroxyl groups present in the fat.

(a) Boil about 10 gms. of the fat with 20 gms. of acetic anhydride for two hours under reflux and cool.

(b) Pour into 500–600 c.c. of hot CO<sub>2</sub>-free water and boil for half an hour.

(c) Draw off the aqueous layer and wash the acetylated product separately with CO<sub>2</sub>-free water until the washings are neutral.

(d) Dry the acetylated product at 100° C. and saponify 5 gms. of it as under 1.

(e) Distil off the alcohol produced and take up the soap in CO<sub>2</sub>-free water.

(f) Add N sulphuric acid to the soap in slight known excess (1 c.c. in excess of the alcoholic alkali originally added).

(g) Warm the solution gently and the fatty acid separates out as an oily layer.

(h) Draw off the aqueous part with a separating funnel.

(i) Wash the fatty acid layer with CO<sub>2</sub>-free water until the washings are neutral to litmus.

(j) Titrate the united aqueous washings and first separated layer with N/10 caustic potash, and deduct the potash equivalent to the excess of acid used in acidifying.

Then the acetyl value is

$$\frac{\text{N/10 KOH used to neutralise acetic acid} \times 5.6}{\text{Wt. of acetylated product taken}}$$



# V.—MILK, BUTTER, AND CHEESE INDUSTRY

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## MILK

The average composition of cow's milk may be taken to be: Water, 87.60; protein, 3.50; fat, 3.40; milk sugar, 4.60; mineral matter or ash, 0.75.

In addition to the above, milk contains small quantities of other substances. Some of these, such as lecithin and nuclein, have an important physiological value, whilst others like urea, cholesterine, hypoxanthine are unimportant.

Milk being a liquid designed for the nutrition of the young contains those materials needed for the development and growth of the organism in its early stages. The proportions in which the various constituents are present in human milk and in the milk of different animals varies somewhat widely, as will be seen from the following table:—

	Woman.	Cow.	Goat.	Sheep.	Horse.	Ass.
Water - - - - -	88.32	87.75	86.34	81.08	90.38	90.35
Fat - - - - -	3.43	3.40	4.25	7.67	1.00	1.30
Protein - - - - -	1.55	3.50	4.40	6.08	1.98	1.80
Milk sugar - - - - -	6.44	4.60	4.26	4.26	6.28	6.20
Salts - - - - -	0.26	0.75	0.75	0.91	0.36	0.35
	100.00	100.00	100.00	100.00	100.00	100.00
Specific gravity - - -	1.032	1.0315	1.033	1.038	1.034	1.033



Comparison of the composition of human milk and other milks will show that considerable differences exist. For the feeding of infants this point is worth attention.

Confining all further remarks to the milk of the cow, it may be said that fresh milk is homogeneous with a bluish yellow colour. The colour varies according to the breed of the cow, Channel Island cattle giving a milk which has a much deeper yellow tint than the milk of other breeds.

Milk has a pleasant, sweetish taste and a characteristic animal smell, but this should not be markedly noticeable. The smell, in fact, may be absent if the milk has been obtained under conditions of extreme care and cleanliness.

When tested with litmus paper milk shows a distinct amphoteric reaction, that is, it turns red litmus paper blue, and blue litmus paper red. The presence in the milk of various neutral and acid phosphates of potassium and calcium as well as carbonates of these two metals causes this reaction. To phenolphthalein milk is acid.

The average specific gravity of milk may be taken to be 1.0315. The freezing point lies below that of pure water, viz.  $-0.553^{\circ}\text{C.}$ , and the boiling point about  $0.2^{\circ}\text{C.}$  higher than water.

Milk when left to stand throws up a layer of cream owing to the rise of the specifically lighter fat globules. In the milk of some breeds of cattle the fat globules are considerably larger than the average, and so rise more quickly. According to Gutzeit the average diameter of the globules in the milk of the shorthorn is  $2.76\ \mu$ , whilst in the Jersey it is  $3.5\ \mu$ .

As regards the number of fat globules in a cubic millimetre of milk varying results have been obtained—average figures are difficult to give, but probably three to five millions is not far wrong.

It has been held by some authorities that the globules of fat are surrounded by some membrane which keeps them apart. This membrane is variously stated to be composed of fibrin, globulin, or casein, whilst Storch isolated from cream, that had been repeatedly washed with water, a material containing 14.77 per cent. of nitrogen which he considered came from the "mucoid membrane" surrounding the fat globules.

The ordinary laws of surface tension seem, however, to satisfactorily explain how the globules are kept apart, and at the present time this is the prevalent view. The work of Morres\* gives strong support to this view.

Considering in detail the constituents of the dry matter, or total solids of milk, the first important class is that of the proteins. There are three of these—casein, albumin, and globulin, and the first represents about 85 per cent. of the total protein of milk. The albumin and the globulin make up the remaining 15 per cent., the latter only being present in very small quantities.

**Casein** is an interesting chemical substance of great economic value; in fresh milk it is in suspension in a finely divided colloidal state. It cannot be separated by filter paper, but filtration through an unglazed earthenware filter leaves the casein (and fat) as a porcelain-like mass on the sides of the filter. This shows that the casein is not dissolved in milk, but is suspended.

The casein from cow's milk is very similar to, although perhaps not identical with, the casein of the milk of other animals.

What is ordinarily called the casein of milk appears to be a compound of casein (which may be regarded as an acid having a basicity of four or six) with lime. The compounds of casein with the alkalies give solutions which are almost clear, with, at the most, a faint opalescence.

Up to the present three compounds of lime and casein have been described, the monocalcium with 0.87 per cent.  $\text{CaO}$ , the dicalcium with 1.55 per cent.  $\text{CaO}$ , and the tricalcium with 2.46 per cent.  $\text{CaO}$ . The existence of the mono- and tricalcium caseinates has been questioned.

Casein is a nucleo-albumin which is distinguished from others of its class by

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\* *Milchwirtschaft Zentralblatt*, 1909, p. 502.



the amount of phosphorus which it contains, and by the effect which rennet has upon it.

The elementary composition of the casein of cow's milk can be seen from the following analyses:—

	Hammarsten.	Tangl.	Burow.	Ellenberger.	Duclaux.
C . . .	52.96	52.69	52.825	53.07	53.00
H . . .	7.05	6.81	7.095	7.13	7.00
O . . .	...	23.141	22.906	22.60	22.65
N . . .	15.65	15.65	15.640	15.64	15.70
P . . .	0.847	0.877	0.808	0.80	0.85
S . . .	0.758	0.832	0.725	0.76	0.80

When milk is acted upon by an acid, or when it sours spontaneously, the casein lime compounds are split up and free casein is precipitated in the form of curd. It appears as though the casein combines with stronger acids, in other words, behaves like a weak base. Van Slyke and Hart describe a casein lactate which they found in sour milk, and similar acid casein compounds are said to arise by the action of organic or mineral acids. More recent work, however, throws doubt upon some of these acid casein compounds. The curdling of milk by rennet may be regarded as taking place in two stages. First the enzyme of rennet splits up the lime casein compounds into paracasein and whey albumin, and coagulation then follows if lime salts are present. The paracasein forms the curd, the whey albumin remains in the whey.

There is thus a fundamental difference between the curd obtained when the milk is coagulated by rennet, and when this takes place under the influence of acids.

The **Albumin** of milk was prepared by Sebelien in a pure state from whey by saturation with magnesium sulphate. It is very similar to blood serum, but has a less specific rotation— $\alpha_D = -37^\circ$  as compared with  $\alpha_D = -57^\circ$  to  $-64^\circ$  for blood serum.

Albumin is soluble in cold water, and coagulates at a temperature of  $70^\circ$ – $72^\circ$  C.

In **Colostrum**, the milk which is given immediately after calving and for several days following, a large percentage of the protein is albumin. Immediately after the birth of the calf the colostrum may contain as much as 16 per cent. of albumin, and this quantity diminishes until after about seventy-two hours the milk again reaches its normal composition. This is shown in a series of analyses by Eugling.

	Number of Hours after Calving.					Ordinary Milk.
	Immedi-ately After.	10 Hours.	24 Hours.	48 Hours.	72 Hours.	
Water . . . . .	73.17	78.77	80.63	85.81	86.64	87.75
Casein . . . . .	2.65	4.28	4.50	3.25	3.33	3.00
Albumin . . . . .	16.56	9.32	6.25	2.31	1.03	0.50
Globulin . . . . .						
Fat . . . . .	3.54	4.66	4.75	4.21	4.08	3.40
Milk sugar . . . . .	3.00	1.42	2.85	3.46	4.10	4.60
Ash . . . . .	1.18	1.55	1.02	0.96	0.82	0.75

As already mentioned, only traces of globulin are present in milk.

**Fat.**—Attention has already been directed to the characteristic globules in which the fat of milk is found. The fat itself is of a pale yellow colour, and is characterised chemically by the glycerides of lower fatty acids which it contains,

and physically by its undercooled state. Upon the chemical properties are based many of the methods used in the analysis of butter. The undercooled condition of the fat is seen when cream is made into butter, for then the solid fat is obtained. The melting point of butter fat lies between  $31^{\circ}$  and  $36^{\circ}$  C. and the sp. gr. is 0.93 at  $15^{\circ}$  C., a fact which accounts for the rising of the fat globules when milk is left to stand.

**Milk Sugar** is the only carbohydrate of importance in milk. See pp. 78a, 78b.

Small quantities of other carbohydrates have from time to time been said to be present also, but their presence lacks confirmation. Milk sugar is a biose, it crystallises with 1 molecule water, and can easily be obtained from whey. Milk sugar is not as sweet as cane sugar, nor is it so soluble in water; 1 part dissolves in 6 parts cold water or  $2\frac{1}{2}$  parts hot water. Milk sugar differs further from cane sugar in not being fermentable with ordinary yeast; it can, however, undergo alcoholic fermentation when a yeast such as that found in "Kephir grains" is used.

Milk sugar reduces Fehling's solution, 0.1 gr of the sugar being equivalent to 1.48 c.c. of Fehling's solution. It is also optically active, and fresh solutions show multirotation. See under Sugar.

**Lactic Acid Fermentation.**—A very typical fermentation which milk sugar undergoes is the lactic acid fermentation. This is brought about by the specific lactic acid bacteria. When the percentage of lactic acid reaches a certain point, *i.e.*, 0.75-0.8 per cent., the development of the bacteria ceases. Before this point is reached the casein is coagulated and the milk, in ordinary language, is sour.

**The Mineral Matter or Ash** contains the salts left after ignition of the milk. As the process of ignition has caused the original milk salts to undergo changes it is difficult to say exactly in what form the salts were originally present in the milk. A comparison of the analysis of the ash of milk (by Schrodts and Hansen) and Söldner's arrangement of the salts of milk in the form in which he judges them to be present, will show the main characteristics.

#### ASH OF MILK (Schrodts and Hansen).

K <sub>2</sub> O	.	-	25.42		Fe <sub>2</sub> O <sub>3</sub>	.	-	0.11
Na <sub>2</sub> O	.	-	10.94		SO <sub>3</sub>	.	-	4.11
CaO	.	-	21.45		P <sub>2</sub> O <sub>5</sub>	.	-	24.11
MgO	.	-	2.54		Cl	.	-	14.60

#### MILK SALTS (Söldner).

Sodium chloride	-	-	-	.	10.62 per cent.
Potassium chloride	-	-	.	-	9.16 "
Monopotassium phosphate	.	.	.	-	12.77 "
Dipotassium phosphate	-	.	.	-	9.22 "
Potassium citrate	-	.	.	-	5.47 "
Dimagnesium phosphate	.	.	.	-	3.71 "
Magnesium citrate	-	.	.	-	4.05 "
Dicalcium phosphate	-	.	.	-	7.42 "
Tricalcium phosphate	-	.	.	-	8.90 "
Calcium citrate	-	-	.	-	23.55 "
Lime combined with the casein	.	-	-	-	5.13 "

The presence of citric acid in milk was proved by Henkel, the quantity being about 0.10-0.15 per cent. The sulphuric acid in the ash comes from the sulphur of the casein and other proteins.

**Analysis of Milk.**—In the sample to be analysed, the fat globules must be evenly distributed through the liquid by vigorous mixing. If the cream has already separated the mixing may be brought about by warming to  $40^{\circ}$  C. and vigorous shaking.

The thoroughly mixed sample, kept sweet if necessary by the addition of a little formalin or powdered bichromate, is subjected to the following tests:—

1. The **Specific Gravity** is taken by means of a special hydrometer called a lactometer, or by a Westphal balance. Average sp. gr. = 1.0315.

2. The **Dirt** is estimated by settling in a long narrow vessel, filtering and weighing; or by filtering through cotton wool and judging the amount of dirt from the appearance of the filter afterwards.



3. **The Total Solids or Dry Matter** determined by evaporating a known quantity of milk to dryness in a flat porcelain or platinum dish, often with the addition of washed and ignited sand or pumice stone. The average weight of total solids = 12.25 per cent.

If the specific gravity  $G$  and fat content  $F$  of a milk are known, the total solids are given by the formula—

$$T = \frac{G}{4} + \frac{6}{5} F + .14.$$

4. **Fat.**—A great many analyses of milk are made for the fat alone; amongst the large number of methods used in the estimation of fat the following are to be recommended:—

(a) Adams' paper coil method, in which a known weight of milk is dried upon a strip of fat-free filter paper, and the paper, after drying, is extracted with ether in a Soxhlet apparatus.

(b) Röse-Gottlieb method. A mixture of ammonia and alcohol is used to dissolve the casein, and the fat is then shaken out with a mixture of ether and petroleum ether. Either the whole of the ether is evaporated and the fat weighed, or an aliquot portion of the ethereal solution is drawn off and evaporated.

(c) Gerber method. This is a modification of the Babcock test. It is accurate, and serves for separated milk if certain precautions are taken. Sulphuric acid (sp. gr. 1.82) is used to dissolve the casein, and to assist the separation of the fat amyl alcohol is added. On whirling the mixture of sulphuric acid, milk, and amyl alcohol in a specially constructed tube or butyrometer placed in a centrifuge, the fat separates out and can be read off on the scale placed upon the narrow part of the tube. 11 c.c. of milk, 10 c.c. of sulphuric acid, and 1 c.c. of amyl alcohol are the quantities used. The centrifuge must have a speed of 1,000 revolutions per minute, and this must be maintained for three or four minutes. In cold weather it may be necessary to warm the butyrometer tube, otherwise the column of fat solidifies, and cannot be read accurately.

Instead of sulphuric acid and amyl alcohol, both of which are objectionable, a mixture of common salt, sodium hydroxide, and Rochelle salt takes the place of the acid, and isobutyl alcohol is used instead of amyl alcohol. This Sal method, as it is called, is quite satisfactory, but as no heat is generated by the mixing of the reagents, the butyrometer tube must always be warmed.

5. It is only exceptionally that the **protein**, the milk sugar, and the mineral matter are estimated in milk. The total protein can be determined by the usual Kjeldahl method, or more accurately by precipitation with copper hydroxide (Ritthausen). Insoluble copper protein compounds are obtained, in which the nitrogen can be estimated.

6. **Milk Sugar** (see p. 78b) is estimated gravimetrically by weighing, either as  $\text{CuO}$  or  $\text{Cu}$ , the  $\text{Cu}_2\text{O}$  precipitated on boiling with Fehling's solution. The polariscope can also be used in the estimation of milk sugar, provided certain precautions are observed (*Scheibe, Milch Zeitung*, 1901, 113).

7. **The Ash or Mineral Matter** is extracted from the residue left after ignition. About 25 g. of milk are evaporated to dryness in a platinum dish, and then carefully ignited. As it is almost impossible to burn away all the carbon without volatilising some of the alkaline chlorides, etc., the ignited mass is extracted with water, filtered, and the residue well washed with warm water. The filtrate containing the milk salts is evaporated to dryness, gently ignited, and weighed. Should the ash of milk weigh less than 0.7 per cent., there would be grounds for suspecting the addition of water.

**The Adulteration of Milk.**—The removal of fat from milk, or the addition to it of water or separated milk, are the two chief adulterations practised. Further, milk to which the "strippings" have not been added may be regarded as adulterated, as is also the mixing of Pasteurised milk with fresh milk.

In this country the Board of Agriculture regulations for the sale of milk fix the minimum limit for butter fat at 3 per cent., and the solids not fat at 8.5 per cent. Milk that falls below these standards is regarded as not being genuine, and milk offered for sale and found to be below the above limits, renders the seller liable to a fine unless he can prove to the satisfaction of the authorities that the milk is genuine.

When the fat in genuine milk falls below 3 per cent., it may be due to various causes, *e.g.*, the length of intervals between milking, the season of the year, cold and wet weather, or insufficient food.

The production of milk on a very large scale is not common in this country. The farms are usually relatively small, and the herds of cows vary from ten or twelve up to one hundred or more. The milk is usually sent to a large dairy company or to a milk dealer in one of the big towns. In the smaller towns the farmer often himself delivers the milk to his customers direct. In Ireland, where the population is smaller, milk is sent to a creamery, often one run on co-operative lines, and there separated, the cream being used for butter, and the separated milk returned to the farmer as food for pigs.

Milk deteriorates very quickly when the conditions under which it is obtained are not those of extreme cleanliness. Hence the producer must exercise continual



vigilance, both during milking and in the cleaning of the vessels into which the milk is put. Apart from pathogenic bacteria, which may in certain circumstances find their way into the milk, there are always large numbers of bacteria which gain admittance. Even before the milk enters the bucket the milk has been contaminated by micro-organisms, chiefly harmless lactic acid bacteria, which were lodged in the ducts of the teats. Milk as secreted by the mammary glands is sterile. Once outside the body milk receives large numbers of bacteria from the air, from the body of the cow, and from the hands and clothing of the milker as a rule. In ordinary fresh milk the number of bacteria per cubic centimetre is never likely to be less than 10,000, and may rise to five or even ten times this amount.

**Cleanliness in Handling Milk.**—There has been much legislation during the last few years, the object of which has been to ensure that the production and distribution of milk is conducted in an hygienic manner. The structure of cowsheds, dairies, and utensils has been laid down. Certain minimum standards have also been fixed for the cleansing of utensils and premises. The health of cows must be supervised by frequent clinical examinations.

Producers of graded milk, working to a high standard of cleanliness, can be relied upon to give good wholesome milk, but there are still milk producers in this country who are never visited by inspectors.

**Bacteriological Control.**—There are many people who strongly advocate the routine examination of milk. While routine bacteriological examination is invaluable in giving the number of bacteria in milk it gives no quick indication of their pathogenicity. More elaborate methods than those normally carried out are required to establish this and so far do not seem to be popular, presumably on account of their slowness. The presence of definite pathogenic bacteria in milk should receive country-wide consideration. The most widely controlled bacillus is that of tuberculosis, although the bacilli *streptococci*, *diphtheriæ*, and *brucella abortus* are also occasionally watched.

The reductase test, which is based upon the decolourisation of a solution of methylene blue, seems well adapted for rapidly giving information as to the relative number of bacteria in a sample of milk. All that is needed is a saturated alcoholic solution of methylene blue, 5 c.c. of which are diluted with 195 c.c. of distilled water. The milk (10 c.c.) is mixed with 1 c.c. of this diluted methylene blue solution, covered with a little paraffin oil, and left to stand at a temperature of 45°–50° C. When decolourisation takes place at the end of an hour the milk is unfit for drinking; if the colour persists for periods between one and three hours the milk may be regarded as having a purity inversely proportional to the time required for decolourisation. A milk that retains its colour for more than three hours is satisfactory.

As an example of the procedure necessary for the control of pathogenic bacteria, the examination for tubercle bacilli will be described. 100 c.c. of milk is divided into four 25 c.c. portions, which are centrifuged for 1 hour at 3000 revs./minute. The tubes are then removed from the machine and the cream layer separated from each tube and the supernatant liquid gently decanted, leaving the sediment. The four lots of sediment are then poured into four smaller tubes and respun for 15 minutes at 3000 revs./minute. The liquid is then decanted from each of the four tubes and the sediment mixed with sterile saline solution to make 3 c.c. This emulsion is then injected into two guinea-pigs and their behaviour watched for several weeks (about 6). The pus formation at the site of injection is examined for tubercle bacilli and the local glands for tuberculous lesions.

The disadvantage of this type of examination is that a very long time is



required, and any milk infected will have been consumed long before the result of the examination is forthcoming. A direct microscopical examination of the deposit from the centrifuge may sometimes be carried out, but results will be difficult to find if the milk examined is from a bulked sample and the concentration of bacilli small. In such a case the inoculation method always has to be used.

When the pus from the inoculated guinea-pig has been obtained, it is smeared upon a microscope slide and dried and fixed by heat. The dried material is then flooded with carbol fuchsin which is not allowed to dry upon the slide. The slide is then washed well with water and immersed in 20 per cent. sulphuric acid for 1 minute, washed with water again, and treated with alcohol for 2 minutes. After washing again with water, counter staining is carried out with Loeffler's methylene blue for 30 seconds. The slide is then washed and dried thoroughly. The tuberculous bacilli show up as red spots on a blue background.

Given healthy animals receiving good food and pure water the wholesomeness of the milk depends largely upon the care bestowed upon the cows, and upon the dairy utensils. Another factor, of course, is the cooling of the milk immediately after milking, so that bacteria in the milk do not rapidly increase. The grooming of the cows, the brushing and washing of the udder before milking, and the provision of a separate room for milking should receive careful attention. The milker should have clean clothes and hands, and the practice of wetting the hands with milk before and during milking should be forbidden; dry milking is a very important factor. The milk should at once be strained through an efficient strainer. The newer strainers, in which the milk first passes through a fine wire sieve and then through cotton wool which can afterwards be thrown away, or a bag of closely woven material which can be thoroughly washed and steamed after each milking, are usually very satisfactory. All vessels used for the reception of milk should first be washed with cold or lukewarm water, then with boiling water, or if a supply of steam is available they may be steamed with the live steam. If such precautions as the above are taken, and the cows are healthy and have been kept under sanitary conditions, and fed with wholesome food and pure water, the milk will be found to satisfy all reasonable requirements. It will keep well, and the producer will soon find that the extra care which he has taken will be repaid by the ready sale of the milk, oftener at a higher price than milk which deposits dirt on standing, and only keeps good for a relatively short time.

Most of the milk produced is consumed as such. However, very large quantities are worked up for **butter and cheese**.

We discuss the manufacture of these products in the next two sections. A very considerable amount of **milk sugar** is also extracted from milk, usually from the whey which is left over after making cheese. The manufacture of milk sugar is described on page 78a.

**Pasteurisation.**—There are still some people who criticise this method of treating milk, but whether their views are correct or not, it remains that at the present time 95 per cent. of London's milk is pasteurised before consumption, and it appears that pasteurisation is well established. The process was invented by Soxhlett in 1886, although the original idea belonged to Pasteur who applied it to wines to prevent abnormal fermentation. Milk that has been pasteurised must comply with the following conditions:—

1. Grade "A" Pasteurised. This must contain not more than 30,000 bacteria per c.c., and no coloform bacillus should be present in  $\frac{1}{10}$  c.c. of the milk prior to the delivery to the consumer.

2. Pasteurised. This must contain not more than 100,000 bacteria per c.c. prior to the delivery to the consumer.

3. Pasteurised milk must have been heated to 145° F.—150° F. for at least half an hour and then immediately cooled to a temperature below 55° F. One



heating only is permitted and the equipment for heating must be satisfactory to the licensing authority.

There is only one method of pasteurisation recognised by the Ministry of Health. This is called the "Holder" process. In this process the milk is held at the pasteurising temperature, in a cylindrical container, for 30 minutes. One of the most satisfactory methods of using the Holder process is to have a number of holders which are filled consecutively in such a way that when the last has been filled the milk has been held for half an hour in the first at a temperature of  $145^{\circ}$ – $150^{\circ}$  C. The containers are then emptied consecutively when each has been held for half an hour exactly. There are various improvements from time to time in the methods of raising the milk to the pasteurising temperature, stirring to avoid cream rising and avoidance of froth. Normally the milk is heated by steam and cooled by water before and after entry into the holder.

A brief description of the other methods of pasteurisation follows.

**Batch Pasteurisation.**—In this method the milk is heated, held at  $145^{\circ}$  C. for 30 minutes, and cooled in the same tank. Low bacterial counts are not obtained with this method and it is rather slow, as cooling the large bulk of milk by a water jacket does not remove heat so efficiently as a proper heat exchanger. The flavour is spoiled by heating by means of a steam jacket above  $145^{\circ}$  C. which is necessary for speed.

**Flash Pasteurisation.**—In this method the milk is heated very quickly to a high temperature (about  $170^{\circ}$  F.) and immediately cooled. The milk is injected at the base of a rotating hollow, vertical cylinder heated to considerably above  $170^{\circ}$  F. The flash pasteurised milk leaves at the upper end of the cylinder. The disadvantages of this method are:

(a) The milk is given a "taste" because it has been in contact with the surface of the cylinder heated considerably above  $170^{\circ}$  C.

(b) The cylinder requires large amounts of steam for heating purposes.

(c) A pump is required to raise the milk up the cylinder. This pumping spoils the texture of the milk and alters the cream line.

(d) Alterations of flow cause the temperature of heating to be altered and a cooked taste may result.

(e) It is doubtful whether all the milk passing up the tube comes into contact with the heated walls and, thus, although the number of bacteria in the milk are reduced, the reduction is unreliable and too dependent upon factors which may not always be constant, such as speed of passage through the machine.

**The Continuous Flow Process.**—This method differs from the Flash pasteurisation method in that the milk passes slowly through jacketed tubes fitted with baffle plates at such a speed that a volume of milk equal to the volume of the apparatus passes through the equipment in 30 minutes. The advantages of such a method are simple design and, therefore, ease of cleaning, close control of temperature, and thus no burning. A disadvantage is that, through turbulent flow and convection currents, it is doubtful whether every particle of the milk remains in the apparatus for the full 30 minutes. Thus some bacteria may escape destruction. The process is probably little more than 50 per cent. efficient.



## BUTTER

Butter can be made from fresh or sour cream or from whole milk. Generally the cream is allowed to sour or ripen before being churned. This gives a larger yield of butter and the flavour is better. The ripening of cream is accelerated by keeping it at a fairly warm temperature, 60°-70° F., and using a starter. The starter may be a pure culture of some lactic acid bacteria, or a little sour milk or butter-milk. First pasteurising the cream and then employing a pure starter is the best means of obtaining cream of the required ripeness, and butter made under these conditions is much more uniform in character.

The composition of butter according to Storch is:—

	From Fresh Cream.	From Ripened Cream.
Water - - - - -	13.03 per cent.	13.78 per cent.
Fat - - - - -	83.75 "	82.97 "
Protein - - - - -	0.64 "	0.84 "
Milk sugar - - - - -	0.35 "	0.39 "
Mineral substances - - - - -	0.14 "	0.16 "
Salt - - - - -	2.09 "	1.86 "

It is thus seen that 83-84 per cent. of butter is fat and the rest is water with small quantities of protein, milk sugar, mineral matter, and 1-2 per cent. of salt which has been added in the making.

The percentage of water in butter is liable to considerable variations, and may reach as much as 20 per cent. In this country 16 per cent. is regarded as the maximum limit.

In the churning of cream the globules lose their spherical shape and collect in larger particles, which usually have a granular form. The evenness of grain of the butter after churning is of importance, and attention is paid by the maker to this point. Well ripened cream, churned at the proper temperature and not too long, gives butter of a good grain.

When the butter has been got into this granular state, it must be thoroughly washed to remove the buttermilk, which otherwise would cause the butter to rapidly become rancid. The temperature at which this is done is also of importance.

When the butter has been washed as free from buttermilk as possible, it is salted, and for this purpose a pure salt is required. It should be free from magnesium salts, otherwise it tends to become moist and then set in hard lumps, which prevents an even distribution of salt through the butter.

The manufacture of butter on a large scale is carried out in precisely the same manner as on a small scale, except that the churns and workers are run by machinery.

In America, in Germany, and to a less extent in Ireland, machines which combine a churn and a butter worker have been introduced into butter factories, so that it is now possible to work, wash, and salt the butter in the same vessel as that in which it was churned. The best known of these machines are the Astra and the Simplex. Attempts have been made to combine a separator with the churn and butter worker, and in Sweden at the present time several of these machines are in use.

Pure butter varies considerably in appearance, colour, taste, and smell, according to the breed of the cow, the food, the time of the year, and method of making. As has already been mentioned in speaking of milk, the fat which is present in the cream in an undercooled state passes into the solid condition on being made into butter. Butter is characterised by the relatively high percentage of glycerides of the lower fatty acids. Other fats contain a much smaller quantity of these glycerides so that a determination of the percentage of lower fatty acids serves as one of the



best methods for the detection of adulteration with some animal fat such as margarine. When the fatty acids are isolated from butter fat it is found that the following are present :—

Butyric acid -	$C_4H_8O_2$ (volatile)	Myristic acid	$C_{14}H_{28}O_2$ (non-volatile)
Caproic „ -	$C_6H_{12}O_2$ „	Palmitic „	$C_{16}H_{32}O_2$ „
Caprylic „ -	$C_8H_{16}O_2$ „	Stearic „	$C_{18}H_{36}O_2$ „
Capric „ -	$C_{10}H_{20}O_2$ „	Arachidic „	$C_{20}H_{40}O_2$ „
Lauric „ -	$C_{12}H_{24}O_2$ (non-volatile)	Oleic „	$C_{18}H_{34}O_2$ „

The proportions in which these acids are present in normal butter are subject to variation, but it is generally found that the glycerides of the first four make up 8-9 per cent. of the total. Almost certainly the glycerides are mixed, that is to say, the glycerin group is combined with different acid radicals, so that butter can hardly be regarded as a mixture of simple triglycerides. There is difficulty in proving this, but Partheil and Velsen, who made an artificial butter from the triglycerides of fatty acids, in the proportion in which they are present in butter, found that it had a higher solidifying point than natural butter.

The specific gravity of pure butter fat at  $100^\circ$  is from 0.865-0.868, the melting point varies from  $28^\circ$ - $34.7^\circ$  C., the solidifying point from  $19^\circ$ - $23^\circ$  C.

Butter fat is insoluble in water, soluble in alcohol, and very soluble in ether, chloroform, benzene, petroleum ether, etc.

The usual analysis of butter is confined to the estimation of the water, the fat, and the salt, and the determination in the pure butter fat of the amounts of soluble fatty acids, insoluble fatty acids, the refractive index, and the iodine value.

**Water.**—Samples having been taken from the bulk by means of a sampler like a cheese borer, they are put into a wide-mouthed stoppered bottle, which is then placed in warm water ( $40^\circ$  C.). The fat, when melted, is shaken vigorously, and about 5 g. are poured into a porcelain dish containing pieces of pumice stone. The dish is then dried at  $100^\circ$  until the weight is constant, or very nearly so. It is not advisable to dry the butter for longer than three hours, for the continued heating tends to change its composition.

A rapid method for the estimation of water is to simply heat the butter in a dish, stirring all the time with a glass rod. When the butter ceases to froth and the casein has a brown colour, all the water has been driven off, and the dish is allowed to cool and is again weighed.

**Fat.**—The dried fat and pumice stone from the previous experiment is transferred to an extraction cartridge, which is then placed in a Soxhlet extractor. The dish from which the butter and pumice have been scraped is washed out well with ether, which is poured over the cartridge, and the extraction is proceeded with in the ordinary way. A layer of extracted cotton wool should be placed on the top of the cartridge to prevent fine particles of pumice stone from being carried over.

The Röse-Gottlieb method is also very useful for the estimation of the fat. Weigh out 2 g. of butter on fat-free paper, and place it in the Gottlieb tube, add warm water to make up to 10 c.c. (as for milk), then 1 c.c. of ammonia, and 10 c.c. of 95 per cent. alcohol. Shake the whole well, cool the tube and shake out with ether and petroleum ether, as in the analysis of milk.

**Salt.**—This can be estimated by dissolving a known weight of butter in ether, to which a little water has been added. The salt dissolves in the water, the fat in the ether, and the two can be separated with a separating funnel. The aqueous solution is then titrated with decinormal silver nitrate, neutral potassium chromate solution being used as the indicator.

Another method is to ignite the butter carefully in a small platinum dish, extract the sodium chloride from the ash with water, and titrate as above.

An examination of the butter fat is necessary to determine whether adulteration with some other fat has taken place. A pure sample of the fat is obtained by melting the butter at a temperature of  $40^\circ$ - $50^\circ$  C., and filtering it through a dry filter.

The refractive index is usually determined with a Wollny-Zeiss butter refractometer. Full details of how to use this instrument are supplied by the makers (Carl Zeiss, Jena), and it will therefore suffice to note that at  $25^\circ$  C. natural butter fat has a refractive index of 49.5-54.0 divisions. At  $40^\circ$  C. the number of divisions on the same instrument is from 40.55-44.4, and fat in exceptional cases 47.



Margarine fat has a higher refractive index—58.6-66.4 divisions at 25° C., and 48.5-52 divisions at 40° C., so that it is possible to detect adulteration with margarine if considerable quantities have been used. The refractive index will hardly serve to detect small quantities, for the figures obtained for genuine butter vary too much. Another substance used in considerable quantities for adulteration of butter is cocoa-nut fat, and this has a refractive index of 33.5-35.5 at 40° C.

There are several well-known chemical tests for the purity of butter fat of which the following deserve notice.

1. **The Reichert-Meissl Value** (p. 64).—Pure butter fat may have a Reichert-Meissl value as low as 20 or as high as 34, but it is seldom that genuine butter falls below 24. Margarine in which a very small quantity of these lower fatty acids is found has a Reichert-Meissl value of 1 or 2, not more as a rule.

2. **The Hehner Value** (p. 64) for genuine butter fat can vary from 85.5-91, the average value is 87.5. In margarine the value is higher.

3. **The Koettstorfer or Saponification Value** (p. 62) is very high for butter, lying between 220.5 and 332 for butter fat. This serves to detect adulteration with many fats whose saponification value is much less.

4. **The Iodine Value** (p. 63).—The iodine value of pure butter fat lies between 25.7 and 49, and it is particularly useful in detecting adulteration with cocoa-nut fat.

The above are the chief tests employed in the chemical examination of butter fat. As margarine is the most usual adulterant of butter, its peculiarities as compared with butter fat have been noticed. See *Margarine Manufacture*, pp. 85-87; also p. 64.

### Colouring of Butter

Butter is nowadays usually coloured, except perhaps during a few of the summer months. The public demand is for a bright yellow butter, so that if the article fails to have the desired colour the sale is prejudiced. The materials used in the colouring of butter are generally harmless in their effect upon the consumer, and the practice is not prohibited by health authorities (see p. 87).

In this country, **Annatto**, which is got from the fruits of the *Bixa orellana* tree, is usually employed. The colouring matter after extraction is dissolved in some vegetable oil. In this condition the annatto is easily incorporated with the butter, and an even yellow colour is obtained. Too much annatto gives a reddish unnatural colour to the butter, and this should be avoided.

**Saffron, curcuma**, extract of marigolds, juice of carrots, are all used as butter colours. Latterly, some of the well-known yellow aniline dyes have been used for colouring butter, and whilst there is no evidence that they are injurious to health in small quantities, it would doubtless be preferable to use one of the vegetable substances previously mentioned.

**Test.**—A very complete scheme to be used in testing the colouring matter in butter has been drawn up by A. R. Leeds (*The Analyst*, 1887), and reference should be made to this paper if full directions for making the various tests are wanted.

**Preservatives.**—Certain preservative materials are used to increase the keeping properties of butter. These preservatives are as a rule similar to those used in preventing milk from turning sour. Boracic acid and its salts are the usual preservatives, and once the fat of the butter has been removed, they can be tested for in the manner already described in the section dealing with milk.

### CHEESE

In its simplest form cheese may be regarded as the solid portion of milk except the milk sugar. It is true that a little milk sugar usually does get into the cheese, but the bulk is not retained. The casein, the fat, and the milk salts make up new cheese, and the nature and composition of the many different kinds of cheese indicate that much variety is possible. In milk the casein is present in a colloidal-like form and is probably a lime-casein compound or compounds. The addition of an acid or of some specific enzyme like the one in rennet causes the casein to split up into paracasein (the curd) and whey.

What changes actually during the coagulation of the casein is not well understood; although Hammersten's explanation of the splitting up of the lime-calcium compound or compounds is generally accepted, it is not easy to give proof. The souring of milk may then be regarded as a cleavage of the lime-casein compounds with the formation of curd and whey.



When rennet is used to curdle milk the curd differs considerably in physical properties from that obtained from milk which has either soured spontaneously or has been treated with an acid.

The souring of milk which takes place ordinarily when it is kept is due to lactic acid which forms as a result of the action of lactic acid bacteria upon the milk sugar. The lactic acid which thereby arises acts upon the lime-casein compounds, decomposing them and causing the precipitation of paracasein in the form of curd. The same effect is produced by the addition of a few drops of a mineral acid to milk.

Cheese is prepared to a small extent from the curd which is obtained when milk sours spontaneously, but it is never good, and cannot be got to ripen properly.

The usual way of making cheese is to allow rennet to act upon milk. The class of cheese which results depends upon the temperature at which the renneting takes place, the acidity of the milk before the rennet is added, the quantity of rennet employed, and the subsequent handling of the curd. Every well-known variety of cheese is prepared according to a definite scheme, the above-mentioned factors being altered in different cases. Rennet contains an enzyme rennin, or chymosin, which brings about the decomposition of the casein of the milk into paracasein and whey albumin. The coagulum in this case differs in chemical and physical properties from the curd which is obtained when an acid acts upon milk. The former contains lime salts, whereas the latter does not, owing to the acid having dissolved the lime. The rennet curd is also more elastic, and not sticky.

Rennet can be bought in powder or fluid form. It is extracted from the lining of the stomach of the calf, in which it is found in considerable quantities. Formerly the stomach was dried, and a piece taken whenever cheese was being made. Now the commercial powders or liquids can be bought very cheaply, and they are more satisfactory, for it is possible to determine their strength, a circumstance which is of great help in the proper making of cheese.

Rennet powder and tablets are usually very active, although the actual amount of enzyme which they contain is very small. One part of rennet powder will often coagulate 250,000 or more parts of milk. The liquids are not so strong, 1 : 10,000 being about the average strength.

In order that cheese of a regular quality may be obtained, it is usual to use a "starter" to ripen the milk before renneting. This "starter," which is similar to that used in ripening cream, is a pure culture of lactic acid, and controls the development of the micro-organisms, with the result that those which are present in the milk are prevented from developing by the activity of the lactic acid bacteria, which increase more rapidly.

To ascertain when the milk is sufficiently ripe for renneting it is usual to make a so-called rennet test, which consists in taking a measured quantity of milk (say 4 oz., or about 140 c.c.) and adding to it a diluted rennet extract ( $\frac{1}{4}$  oz., or 5 c.c.). The mixture is then stirred and the time taken for coagulation is noted in seconds. For cheddar cheese the time is from 45-60 seconds. When the milk coagulates more slowly than this it is an indication that the milk is not sufficiently ripe.

There are so many different kinds of cheese that particulars of their manufacture would necessitate more space than is available in this article, and reference should, therefore, be made to books which deal with cheese-making from the practical side. To properly understand the chemical changes that take place in making cheese, the following is a brief description of the manufacture of **cheddar cheese**.

Great care is exercised in getting pure milk, for it is impossible to make good cheese if the milk is dirty.

The night's milk is run into a jacketed vat, the next morning the cream is skimmed off, mixed with the proper proportion of starter and then returned to the vat. The fresh morning's milk is then added and the temperature is carefully regulated to about 85° F. After standing for some time the rennet test is made and if the milk is found to be of the desired acidity, the whole of it is renneted. The amount of rennet to be added depends upon its strength, but usually 1 oz. to 20 gals. of milk is about right; this represents as a rule .04 per cent. of rennet. After the milk has been stirred it is left to coagulate, which should take place in about three-quarters of an hour. The curd must then be tested (usually this is done with the finger), and if ready, it is cut with special knives so that the curd is left in small dice-like pieces. The temperature of the vat is then gradually raised to about 102° F. and the contents stirred. This heating and stirring makes the curd firmer, so that the whey is expelled. A test is usually made to ascertain if the curd is sufficiently ripe. A small piece of curd, well pressed with the hand, is taken, placed against a hot iron and then with-



drawn. The curd draws out into threads and the length of these threads enables the cheese-maker to decide whether the curd is sufficiently ripe for the purpose. The longer the threads, the riper the curd.

If the ripeness is judged to be satisfactory the whey is run off, and the curd transferred to coolers, where it "mats" and forms a solid block, and acidity develops rapidly. The next operation is the grinding of the curd followed by salting, after which it is packed into cheese moulds and put into the press. Considerable pressure (1-1½ tons) has to be used before the cheese is taken from the press, but at first a pressure of ½ cwt. or less is needed. The subsequent removal of the cheese from the mould, the banding, etc., are technical operations which are employed before it is removed to the ripening room. In this room the cheese undergoes many changes which are known collectively as "ripening."

The process of ripening is a very important factor in cheese-making, for a freshly-made cheese is insipid and indigestible. During the process of ripening a large proportion (38 per cent.) of the casein is rendered soluble. The changes that take place during ripening are not well understood nor has it been satisfactorily explained what causes them. Without question, both bacteria and enzymes take part in the process, and the lactic acid bacteria and others which flourish in an acid medium are important factors. The enzymes, *i.e.*, rennin and pepsin (both of which come from the rennet), must be reckoned with, and, according to Babcock and Russell, a specific enzyme found in milk, and called by them galactose, also assists. The chemical changes which take place during ripening are very interesting, although as yet they remain unexplained in some cases, but the results are seen in the alterations brought about in the casein. The casein, in fact, undergoes a considerable degree of change, and instead of remaining as an elastic curd it becomes more and more plastic until ultimately it may be largely converted into simpler nitrogenous compounds such as albumoses, peptones, and even relatively simple substances such as leucine, tyrosine, etc. There are also present in well-ripened cheese a number of decomposition products such as alanine, glutamic acid, lysine, putrescine, cadaverine, and ammonia.

The milk sugar present in small quantities in new cheese soon undergoes lactic acid fermentation, and the gas which is formed causes holes which are a characteristic feature of some kinds of cheese.

**Soft Cheese.**—In addition to the different varieties of hard pressed cheese there are a large number of types of soft cheese made either from whole milk or milk to which more or less cream has been added. Some of these cheeses are eaten fresh, whilst others are allowed to ripen for three to six weeks.

**Colouring of Cheese.**—In some districts cheese is coloured more or less highly with annatto, which is used in aqueous solution, instead of dissolved in oil as in the case of butter.

**Adulteration of Cheese.**—The direct adulteration of cheese may be said to be limited to the extraction of the butter fat from the milk before the cheese is made, and the substitution of some other and cheaper fat. Indirectly adulteration of cheese may be said to take place when some fat is removed from the milk, and the cheese is described and sold as having been made from whole milk.

**Analysis of Cheese.**—An average sample, taken with a cheese borer, is rapidly ground up in a mortar, and (1) the **water estimated** by drying first at ordinary temperatures in a vacuum desiccator over  $H_2SO_4$ , then at  $100^\circ$  for eight hours in the steam oven. Soft cheese is ground with sand before drying. (2) **The fat** is estimated by first drying with sand in a porcelain basin, and then extracting with ether for two hours in a Soxhlet apparatus. The method is not very satisfactory, and Weibull (*Zeit. für Untersuchung der Nahr- und Genussmittel*, 1909), and Siegfeld (*Milch Zeitung*, 1904) have devised more rapid and accurate methods, for details of which the originals should be consulted.

(3) **Protein.**—In new cheese the casein has undergone little change, but in one that has ripened considerably a good deal of it has become converted into simpler nitrogenous compounds, some of which are soluble in water.

To distinguish between the soluble and the insoluble protein of a cheese a water extract is made, filtered, and the protein and basic decomposition products in the extract are precipitated by phosphotungstic acid. The precipitate is collected, washed, and the nitrogen in it determined by Kjeldahl's method. To find out how much of this soluble nitrogen is present as basic decomposition compounds, a portion of the original filtered aqueous extract is distilled with magnesia, and the ammonia estimated by passing it into standard acid.

The total water-soluble nitrogenous compounds are determined in a known quantity of the original filtered extract by evaporating it to dryness, and analysing by Kjeldahl's method. Thus the figures obtained in this last experiment, minus the amount of nitrogen present as protein and that present as ammoniacal compounds, represent the amide nitrogenous substances.

Other means of estimating the amount of protein are also used, *e.g.*, Ritthausen's copper precipitation method, but the above is complete and satisfactory.

The total nitrogenous matter, soluble and insoluble, present in cheese can be estimated by determining the nitrogen present in 2-3 g. of the original substance.

**Adulteration.**—Adulteration of cheese is almost entirely restricted to removal of fat. With modern emulsifying machines it is possible to substitute some cheaper fat for the valuable butter fat extracted from the milk from which the cheese was made. **Margarine cheese** is a product which has been made in this way (see p. 87).

To detect this form of adulteration, the fat of the cheese is isolated, and then examined as though it were butter. A determination of the Reichert-Meissl value, the refractive index, and other tests employed in the detection of margarine in butter are used. To obtain sufficient fat for the purpose, the cheese is ground up with very dilute sulphuric acid, and the liquid afterwards whirled in the centrifuge; this serves to separate the fat, which is pipetted off and purified by melting and filtering through a dry filter paper.

**Statistics.**—The quantities of **butter** and **cheese** imported into the United Kingdom are :—

	1906.	1910.	Value in 1910.
	Cwt.	Cwt.	
Butter - - - -	4,300,000	4,300,000	£24,500,000
Cheese - - - -	2,600,000	2,500,000	6,800,000

Against this there were in 1910 *exported* 9,000 cwt. butter (*value* £56,000) and 8,000 cwt. cheese (*value* £38,000).

The corresponding figures for the United States are :—

#### IMPORTED IN 1910.

Butter and butter substitutes - - -	-	1,360,000 lbs. (value, \$298,000.
Cheese and cheese substitutes - - -	-	40,817,000 lbs. (value, \$7,053,000).
Cream - - - - -	-	732,000 galls. (value, 578,000.

#### EXPORTED IN 1910.

Butter and butter substitutes - - -	-	3,140,000 lbs. (value, \$785,000.
Cheese and cheese substitutes - - -	-	2,846,000 lbs. ( „ \$441,000.

For modern statistics see Appendix III.



## THE MANUFACTURE OF MILK SUGAR

BY GEOFFREY MARTIN, Ph.D., D.Sc.

## LITERATURE

G. ZIRN.—*Milch Zeitung*, 1895, 481, 497. The processes here described are still in use.

When milk is used for making cheese (see p. 75) or casein (p. 68), the whey which is left can be used for the manufacture of milk sugar. The solid matter in whey can be taken as: Milk sugar, 4.6-5.0 per cent.; protein (chiefly albumin), 1.0; fat, 0.3; mineral substances, 0.6. When whey is boiled the albumen coagulates, and if the boiling is continued nearly to dryness an impure variety of milk sugar is obtained. This crude milk sugar, which is made in parts of Switzerland, and there known as "Schottensick," contains 85 per cent. of milk sugar, 10 per cent. of water, and nearly 5 per cent. of mineral matter, along with small amounts of protein and fat. When large quantities of whey are obtained, as in cheese or casein factories, the evaporation of the whey is carried out in *vacuum pans*.

The whey must be worked as quickly as possible, otherwise fermentation may set in, the milk sugar being partially decomposed into lactic acid, which then inverts the milk sugar into lactose, thereby occasioning a serious loss. The addition of a little sodium carbonate solution so as to neutralise most of the acid—care being taken to allow the liquid to remain very faintly acid—tends to prevent loss of milk sugar by inversion. The addition of *formalin* (100 g. to every 1,000 l. of whey) also acts well, but is somewhat expensive.

Sour milk must be carefully neutralised before concentrating.

The evaporation takes place at 60°-70° C. in vacuum pans (best in double-effect pans in order to economise steam), the evaporation taking place in such a way that as the water boils away fresh whey is allowed to flow in continually at such a rate as to maintain the level of the liquid constant. The liquid thus gradually concentrates to 30°-32° Bé., when it contains 60 per cent. of solid matter; it is then run out into iron crystallising tanks of 700 l. capacity and allowed to cool. In summer the cooling must be hastened by surrounding the tank with cold water or by immersing cooling coils in it. The temperature must fall from 60° C. to 20° C. in twenty-four hours. A coarse-grained pasty mass of crude milk sugar crystals separates at this stage. The mass is centrifuged (using same apparatus as is employed in beet sugar manufacture, pp. 162-163). 100 parts of whey yield 3.6-4.3 per cent. of crude yellow sugar, which contains 88 per cent. milk sugar, 12 per cent. water, salts, proteids, etc.

There passes away from the centrifugal machines about one-third of the original mass as a syrup still containing much milk sugar, which is often extracted by passing in live steam to the liquid of density 15° Bé.; this coagulates the albumen, which collects on the surface, and which is left behind as a cake when the syrup is run off; the cake is pressed between cloth, ground, mixed with nitrogen-poor material, e.g., potatoes, turnips, etc., and used as a food for pigs.

The syrup at 35° Bé. (warm), thus freed from albumen, is once more run into the vacuum pans, concentrated, allowed to crystallise (after standing some days in well-cooled vessels), diluted with water, and centrifuged, when a further yield of 0.3-0.7 per cent. of crude milk sugar is obtained. Total yield of crude milk sugar is about 4.35 per cent.

The liquid from this second crop of milk sugar is used as a manure. It still contains some albumin and non-crystallisable sugars, but it cannot be used for feeding pigs as it causes diarrhoea. It has been worked for lactic acid and calcium phosphate.

Another way to obtain the crude milk sugar is to neutralise, or nearly so, the acid of the whey with sodium or ammonium carbonate, then boil, when the coagulated albumen rises to the surface along with the fat, in the form of a porous scum. This is skimmed off and the liquid can easily be evaporated in a vacuum pan.

**Purification of the Milk Sugar.**—The crude yellow milk sugar, obtained as above described, is sometimes dried and sold as such. More often it is sent to refineries and worked up into pure white milk sugar. The crude milk sugar is dissolved at 50° C. with stirring in a steam-headed copper boiler. The solution contains 24-27 per cent. milk sugar (13-15° Bé.). Animal charcoal and 2 per cent. of acetic acid is added (to precipitate albumen), the solution warmed nearly to the boiling point, some magnesium sulphate is added (to precipitate phosphoric acid), and the liquid is boiled for some minutes. The liquid foams. The temperature rises to 105° C. A sediment collects at the bottom. The liquid is pumped upwards (by a centrifugal pump) into a copper vessel covered with wood, and then allowed to flow downwards through filter presses.

The precipitate is rich in P. and N. and is a valuable manure. The clear liquid, of a yellowish tint, is concentrated in vacuum apparatus to 35° Bé. (65 per cent. sugar). Any foaming is stopped by adding a little fat and increasing the pressure.

Finally the concentrated liquid is run into iron crystallising vessels, cooled, and the separated milk sugar is centrifuged. The mother liquors are worked for further crops of sugar. The milk sugar thus obtained is further refined by dissolving in water (to 15° Bé.), heated to boiling, aluminium sulphate is added, the liquid is filter pressed, concentrated to 32° Bé., cooled in copper (not iron) crystallising vessels, centrifuged, and the resulting white sugar is dried in rotating inclined cylinders, in a stream of hot air, cooled, ground, and packed for export.

Milk sugar is sometimes adulterated with other sugars and sometimes with mineral substances. The former are detected by the change in the rotatory power, particularly in what is termed the birotation ratio, which is the initial rotation, that obtained immediately after the solution is made, divided by the rotation at the end of twenty-four hours. The increase in weight of the ash above the normal (0.035-0.05) denotes mineral adulteration.

Milk sugar, although expensive, is often used in brewing, as it is not fermentable by ordinary yeast, and so remains in the finished product as unchanged carbohydrate, thereby increasing the "extract" of the beer. Also sold as a constituent for children's food.

#### Determination of Milk Sugar (lactose)

1. The percentage of milk sugar may be found by difference, *e.g.*, by subtracting the total percentage of fats protein and ash from the percentage of total solids.

2. Fehling's solution method.—Mix 10 c.c. of the milk to be examined with 100 c.c. of water and add 1.5 c.c. of 10 per cent. acetic acid solution. Boil. Filter off the whey from the solid matter and make up to 100 c.c. Place 20 c.c. in a burette. Five c.c. of both Fehling's solution (A and B) are placed in a flask, diluted with 30 c.c. of water and boiled. Two c.c. of the whey are run into the flask and the contents boiled until the colour fades. Another 2 c.c. is added and the mixture again boiled—and so on until the colour has completely faded. Smaller quantities of whey are run in towards the end of the reaction. Now 10 c.c. of *standard* Fehling's solution requires 0.0678 gm. of milk sugar for reduction. Thus the weight of milk sugar in the volume of milk taken is readily calculated.

Harvey and Hill's "Milk Production and Control" gives a third method employing Benedict's solution.

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## VI. INDUSTRIAL CASEIN

BY G. MARTIN, Ph.D., D.Sc.

REVISED BY E. I. COOKE, M.A., B.Sc., A.R.I.C.

### LITERATURE

- L. MIDDLETON NASH.—Art. "Casein" in *Thorpe's Dict. Chem.* (1912).  
 R. SCHERER.—"Casein." London, 1906.  
 GEOFFREY MARTIN.—"Industrial Casein," *Chemical World*, 1612, I. 353.  
 LUTERMEISTER AND BROWNE.—"Casein and its Industrial Applications." Reinhold, 1939.

The chemical nature of casein, as well as its use in the production of cheese has been discussed in the preceding article.

**Manufacture.**—The machine-separated milk used for casein manufacture, containing 3 per cent. casein, 0.4 per cent. milk albumen, 0.15 per cent. fat, 4.7 per cent. sugar, 0.7 per cent. minerals, must be as *fat-free* as possible. Milk rich in colostrum (taken from cows soon after calving) is unsuitable, as it yields soft curds which squeeze through filter cloths and hold much water. Milk containing coagulated albumen (*i.e.*, boiled or highly heated milk) also yields a curd difficult to work.

Industrial casein is usually precipitated by gradually running in the proper amount of *dilute sulphuric acid*, with constant stirring, into the milk until it becomes clear yellow with separation of the *curd*, which is drained, washed with cold  $H_2O$ , pressed (or centrifuged), broken up and dried—best in a Passburg vacuum drier, but also on trays in hot air drying chambers or cylinders. Great care must be taken not to heat too strongly or the casein dries to a dark colour. The dry casein is ground and packed for export.

However, the curd may also be precipitated by *HCl*, *phosphoric acid*, *lactic acid*, *acetic* or *citric acid*, by *rennet*, by *self-souring*, and by electrolysing milk at  $120^{\circ} F$ . with Ni or C electrodes. In order to render the curd *fat-free and white*, the precipitated curd, after well washing and pressing, is sometimes stirred to a pulp with water (100 curd to 50 water), and then steamed for twenty-five to thirty minutes in a wooden vat with about 150 parts of a 1 per cent. solution of soda. This is to remove lactic acid and butter fat. After heating, the mass forms a thin milky fluid, which is transferred to a separate vessel to cool, and is then precipitated with dilute  $HNO_3$ . The precipitated casein collects at the bottom, the supernatant liquor is run off, and the casein rinsed with water, settled, and water decanted, the washings being repeated until the wash waters are neutral. The casein is then drained on filter cloths, pressed, and dried on trays in drying chambers at  $120^{\circ}$ - $140^{\circ} F$ . One hundred parts of curd yield 45 parts purified casein, free from lactic acid and butter fat.

Among other methods proposed for preparing industrial casein, the following may be mentioned:—

1. The curd is precipitated from the skimmed milk with dilute  $H_2SO_4$ , the yellowish product redissolved in alkali (sod. bicarbonate), and reprecipitated with dilute acetic acid (German Patent, 135,350).
2. The casein is precipitated by leading  $SO_2$  gas into milk warmed at  $50^{\circ}$ - $70^{\circ} C$ . The process is complete in a few minutes, the time taken being so short that there is no danger of inversion occurring (German Patent, 184,300).
3. A fat-free casein is obtained by mixing decreamed milk with alkali, warming, removing the fat by centrifuging, and then precipitating casein in the ordinary way with acid (German Patent, 135,745).

**Uses.**—Industrial casein is used (1) as a painting material; (2) as a mucilage and cement; (3) in the preparation of plastic masses, forming substitutes for horn, celluloid, ivory, etc., and especially for "galalith"; (4) as a dressing and colour-fixing medium in the paper and textile industries; (6) as a food stuff; (7) for "fining" wine. This is cheaper and better than albumen. See p. 245.

**Statistics.**—In 1910 England imported casein of value £54,000. The export reached £21,000. The United States in 1910 imported 3,769,000 lbs. of casein of value \$304,000. The chief firm in England is *Erinoid, Ltd.* See also Appendix III.

**Casein Glue** (see Glue, p. 596).—Casein can be converted into an excellent glue by stirring it up with 400 per cent. distilled water and  $3\frac{1}{2}$  per cent.



sod. bicarbonate, standing for five to six hours, and adding an antiseptic to prevent mould. Sometimes shellac is added. The glue is now ready for use. Such glues can be applied cold.

Very often the casein is dissolved in borax, soda, or ammonia. The applied casein glue is made insoluble by formaldehyde. A *waterproof* glue is obtained by dissolving casein in lime.

In the woodworking trades casein glues threaten to displace ordinary gelatine glues because casein glues can be applied cold (so that all the trouble of melting the glue is avoided), can be made waterproof, and by their use certain delicate effects are attainable in veneering work which are impossible with gelatine glue, since the latter must be applied *hot*, and is not waterproof.

**Casein as a Sizing Material.**—Casein is widely used for sizing paper and similar materials (see **Paper**).

It is dissolved in alkaline solutions, and mixed into the paper pulp. The process is especially useful when the paper pulp has to be moulded or pressed into relief forms; as the casein size is very resistant to heat or moisture. Extremely beautiful art papers are sized with casein, and some photographic papers are also casein sized, the papers being extremely resistant to heat and moisture, and thus keep well in the tropics. The leather and textile industries also employ casein for "dressing" and "finishing" purposes. The great advantage of casein over gelatine is that it is entirely precipitated by the subsequent addition of alum, whereas most of the gelatine is lost in the back water. In the printing of materials a casein product containing silicic acid is used instead of egg-albumen; it is prepared by dissolving the casein by heating with dilute  $\text{NH}_3$ , adding sodium or potassium silicate, and adding phosphoric or acetic acid until the whole, which first solidifies, again becomes fluid (German Patent, 161,842).

**Casein Water Paints.**—See under **Paints**, p. 512.

**Manufacture of Bone Substitutes from Casein.**—Casein when mixed with formaldehyde gives an insoluble horn-like product, which is used as a bone, horn, and celluloid substitute. See under **Celluloid** substitutes and **Galalith**, p. 210.

**Casein Food Stuffs** (see **Cheese**, **Milk Powders**, and **Guttmann's Nutrient Milk Flour**) consist of casein mixed with carbohydrates, such as gluten-free oatmeal, and a small quantity of aromatic substances.

**Visem** is a more recent similar food, containing lecithin and salts of glycono-phosphoric acid. **Sanatogen** is said to consist of 95 per cent. casein and 5 per cent. of sodium glycono-phosphate. White powder, soluble in  $\text{H}_2\text{O}$ , fat-free; lactose-free (see German Patents, 98,177, 1898; 99,092, 1897; 99,093, 1897; 99,094, 1897; 152,380, 1903; 152,450, 1903; 118,656, 1899. See also *Chem. Ztg.*, 1899, 371; 1900, 538, 718). **Eulactol** is a white powder prepared by evaporating milk *in vacuo* at 98° F.; it contains 33.25 per cent. albumen, 46.3 per cent. fat, 14.3 per cent. of carbohydrates, and 4.3 per cent. saline matter (see D.R. Patent, 98,441; *Chem. Ztg.*, 1899, 851).

**Plasmon** (casein) is an albuminoid preparation from milk, occurring as a yellowish white powder containing 75-80 per cent. albumin, 5-7 per cent.  $\text{Na}_2\text{CO}_3$ , 5-10 per cent. fat and milk sugar—very assimilable (see German Patent, 100,977, 1898. *Chem. Ztg.*, 1900, 538, 718. *Chem. Centralblatt*, 1899, II., 533, 1130; 1900, I., 677, 828).

**Dr Riegel's Milk Albumen** is said to contain 86 per cent. albumin, 8.2 per cent. water, 0.31 per cent. fat, 17.4 per cent. mineral matter. The curd is precipitated from the milk by ethyl sulphuric acid.

**Eucasein** is a casein ammonium compound, soluble in water (see *Chem. Ztg.*, 1899, 851; D.R. Patent, 84,682, 1895; 108,053, 1897).

**Nutrose** is a *sodium caseinate* (see German Patents, 85,057, 1894, and 89,142).

For **Sanose** see *Chem. Ztg.*, 1898, 686; 1899, 371; *Chem. Centralblatt*, 1899, I., 1294.

For **Casein** foods, separated from milk by citric acid and containing calcium phosphates, see German Patents, 115,958; 123,622, 1898; 137,000, 1901; 122,458, 1899.

**Vi-Casein**, a soluble sodium caseinate, contains 76-78 per cent. proteins, is free from milk sugar (nearly), and so is used for diabetic patients.

**Acknowledgment.**—The author's best thanks are due to *Mr L. Myddelton Nash* for much valuable advice on this subject.

**Casein in Plastics.**—See p. 619 *et seq.*



## VII.—CONDENSED MILK AND MILK POWDERS

By E. I. COOKE, M.A., B.Sc., A.R.I.C.

### INTRODUCTION

The practice of condensing milk in the general sense to either smaller liquid volume or to a powder has been carried out for hundreds of years. References to milk powder date back to the thirteenth century. Marco Polo, the celebrated Venetian traveller, rose to Kublai Khan's \* favour, and was employed in various important capacities. On returning to Greece he reported that the soldiers of Genghis Khan carried dried milk as part of their ration.

Nicolas Ceppert, the French scientist, in 1810, made milk tablets from milk dried by a current of air.

Grimwode issued the first British patent in 1855.

The composition of milk and its physical characteristics have already been dealt with in section V (p. 67).

The condensing and drying of milk has been known from earliest times. From the crude, unhygienic method of blowing air of doubtful purity through hot milk has developed the method of vacuum evaporation of the water at temperatures of the order of 40° C.

Early attempts at powdering milk involved bulk evaporation to dryness, producing a milk of very inferior quality. In processes now in use the milk is evaporated in the form of a spray or film in contact with the heating medium or heating surface for a very short time.

**Sweetened Condensed Milk.**—Sweetened condensed milk averages  $2\frac{1}{2}$  to 1 condensation. It contains some added sucrose and sometimes dextrose. Total added sugar may average 40–45 per cent. of the total weight of the finished product. The British standard calls for not less than 9.2 per cent. milk fat and 31.0 per cent. total solids. Similar figures for U.S.A. are 8.5 and 28 per cent.

The following diagram (p. 82) gives a flow line for the manufacture of sweetened condensed milk.

Milk from the weigh tanks (A) flows over the cooler (B) into tanks (C) where a sample is analysed into fat and solids not fat. Pump (E) causes the standardised milk to flow from (C) into supply tank (D) whence it flows to (F) and (G) where forewarming takes place. Sterilisation also takes place in (G). Hot milk passes into (H) where it is mixed with sugar. On leaving (H) the sugar-laden milk passes into the vacuum pan (I). Samples of the condensed milk may be removed through (K) into drop tanks (L) where it is standardised for total solids. Pump (M) then forces the standardised milk through cooling coils (N). On leaving the coils the condensed milk passes into the forced crystallisation tanks (O) from which it passes to the filling machine (P) where the tins are filled and sealed.

For a description more detailed than can be entertained here, the reader is referred to Hunziker's excellent book.

Sweetened condensed milk is marketed in hermetically sealed tins for the retail trade. Bulk deliveries are packed in steel drums and wooden barrels, although the latter hardly seem sufficiently hygienic for long storage.

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\* A Mongol Emperor.

**Evaporated Milk.**—Evaporated milk is cows' milk condensed *in vacuo* at ratio of  $2\frac{1}{2}$  or 2 to 1. The British standard calls for 9 per cent. fat and 30 per cent. total solids in the finished product, and the U.S. standard requires 7.9 per cent. fat and 25.9 per cent. total solids.

The equipment used for the production of evaporated milk is very similar to that used in the production of sweetened condensed milk, except that no equipment for the solution of sugar is required and that a homogeniser is used after condensing to mix the cream so that little separation takes place. At the end of the condensing process the milk is sealed in cans which are then sterilised by subjecting them to steam under pressure.

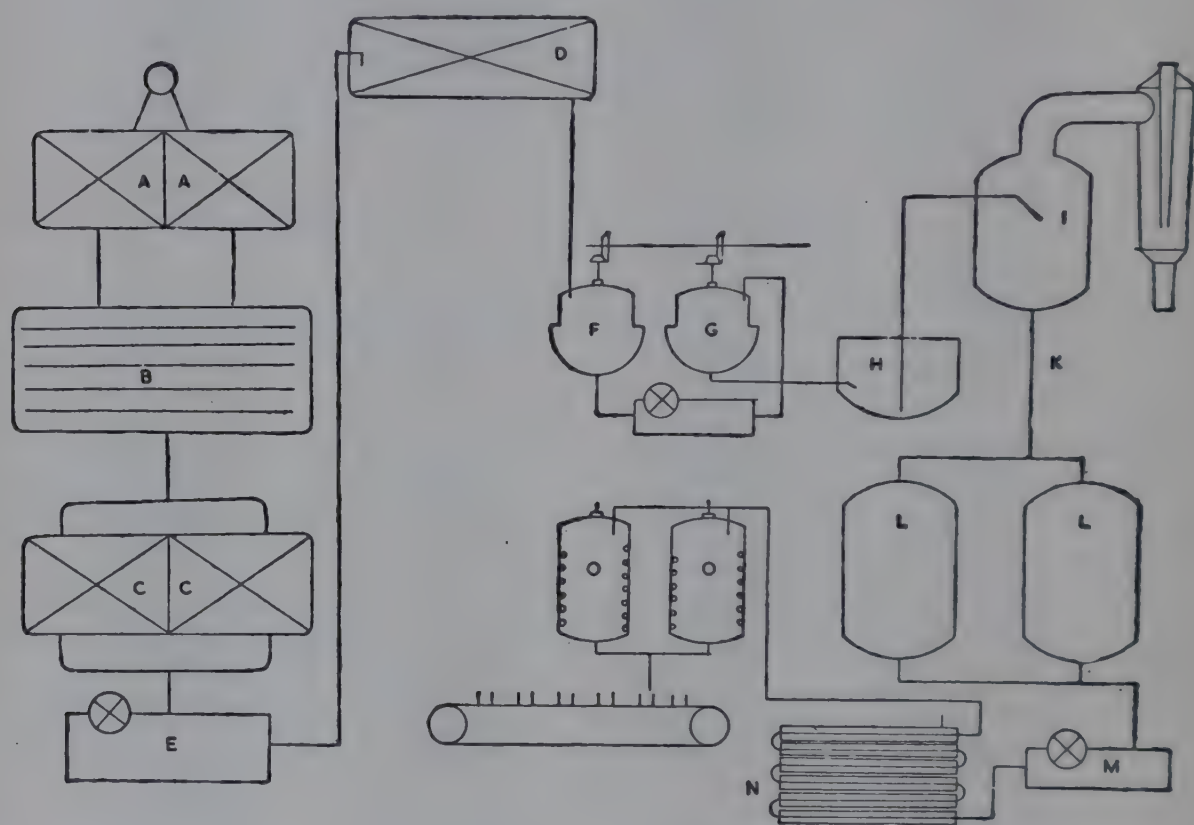


FIG. 21.—The Preparation of Sweetened Condensed Milk.

Evaporated milk usually passes through an irradiator on its way from the vacuum pan to the homogeniser. By this process the vitamin D content of the milk is increased from the natural content. Cholesterol, a provitamin, already present in milk, is changed in such a manner as to have the properties of vitamin D, when the milk is irradiated with ultra-violet light. An electric arc is used for this purpose in the U.S. Mercury vapour arcs are also used. The milk flows down the inside of a hollow cylinder, in the centre of which is suspended the source of ultra-violet light.

Vitamin D in concentrated form in vegetable oil is now often added to milk instead of irradiation.

The following table shows the approximate compositions of sweetened condensed and evaporated milks:—



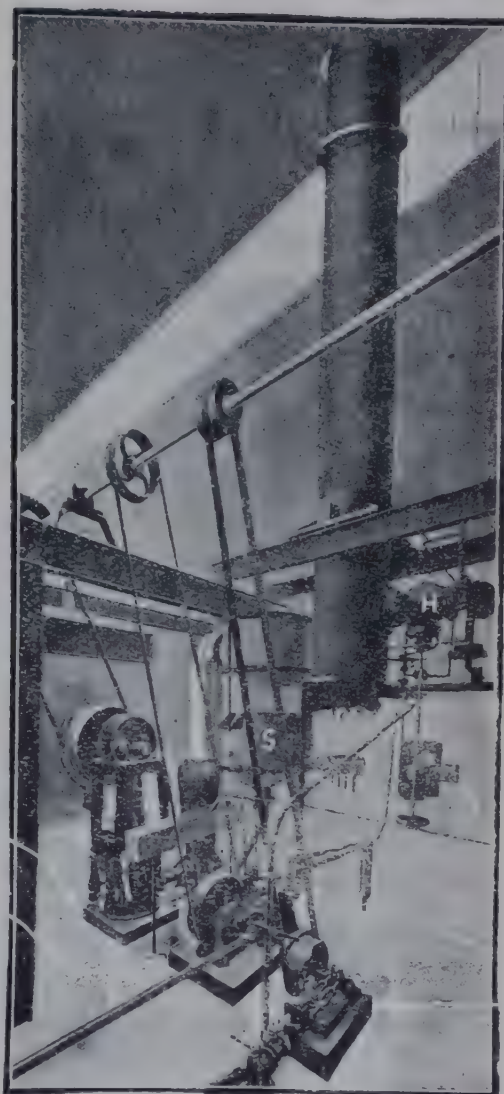
# A CONDENSED MILK INSTALLATION.



A

Pump for Vacuum.

Pump for Extracting Condensed Milk.



Steam.

Pump for Feeding Condensed Milk.

B

FIG. 21a.—Kestner Installation in Condensed Milk Factory.

**Kestner Evaporator for Condensed Milk.**—A high vacuum is applied at C by means of a pump. The milk is forced by another pump into a feed box B, whence it passes up a number of 20 ft. tubes G, which are surrounded by steam, which enters the calandria or steam box by H, the condensed water running away at L. The steam heats the milk and it rushes up the tubes G in the form of a film with a hollow core of vapour, and arrives in the upper box above the top tube plate. The liquor and vapour then pass down the tubes D, similarly heated, the liquor passing as a film down the sides of the tube, and the vapour, which is travelling at a high velocity, forms a core in the centre of the tube.

Both liquor and vapour pass tangentially into the separator S, the rotating action set up completely separating by centrifugal action the liquor from the vapour, so that the vapour passes out at C and the liquor is pumped out (against the vacuum prevailing in S) at P by a pump shown in the photograph.

The velocity of the liquor through the tubes is so great that it only remains in contact with the heating surface for a few seconds before arriving at separator S. There is, therefore, no burning of the liquor.





Components	Sweetened Condensed Milk (British) Per cent.	Evaporated Milk (British) Per cent.
Water . .	26.0	69
Fat. . .	9.0	9.0
Protein . .	8.5	8.3
Milk sugar .	12.2	12.0
Cane sugar .	42.5	0.0
Ash . .	1.8	1.7

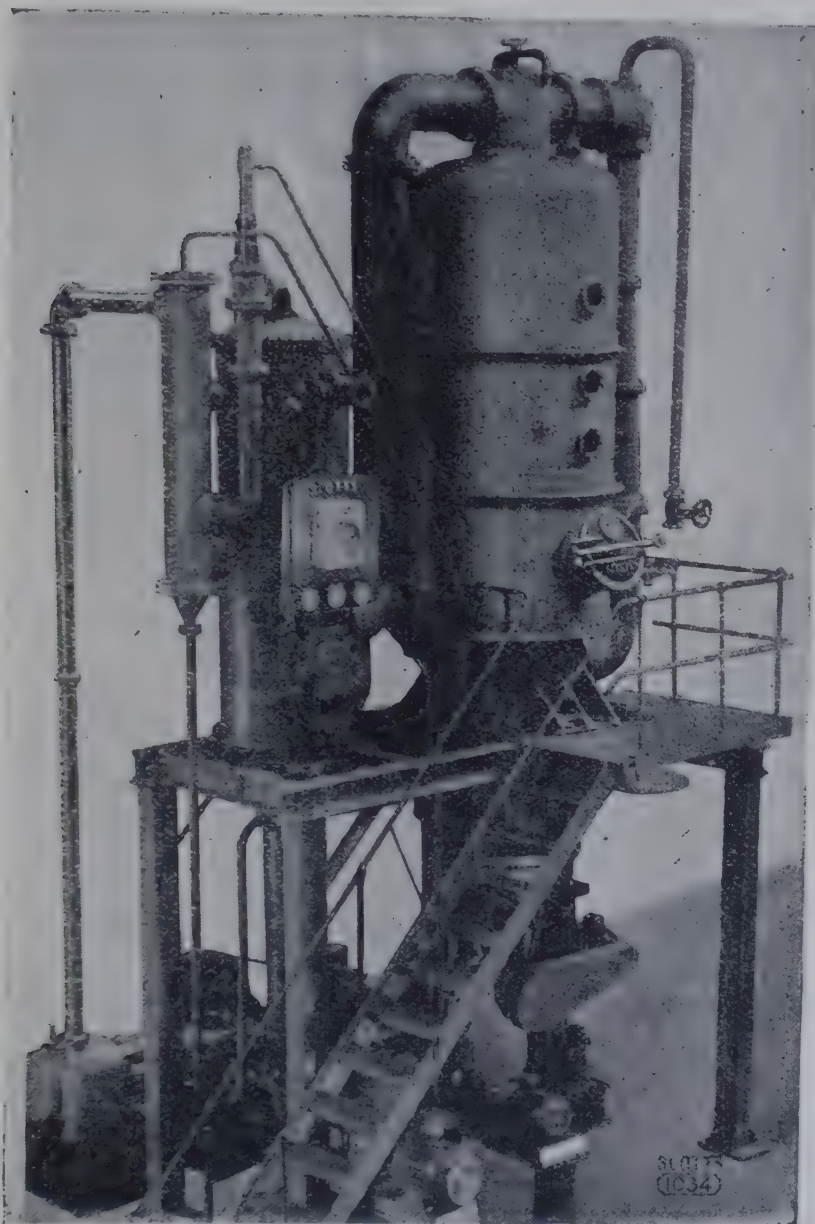


FIG. 22.—A modern Vacuum Evaporator incorporating the Scott Forced Circulation Unit and Thermocompression System. These two modern developments give high heat transfer and save steam in a single effect comparable with that of a double effect.

**Milk Powders.**—The following methods have been used to dry milk (besides the methods originally tried in which a large bulk of milk was evaporated to dryness—resulting in a very inferior quality milk):—

1. Drying by means of cold.
  - (a) Freezing out water and centrifuging.
  - (b) Freezing milk and sublimation under vacuum.
2. Drying by means of heat.
  - (a) Dough or paste drying.
  - (b) Film drying in vacuum or in air.
  - (c) Flake drying in the atmosphere.
  - (d) Spray drying by compressed air, pressure spray, or by centrifugal spray.

Drying by means of freezing out the water and centrifuging was patented by McIntyre in 1894. The milk solids-ice mixture is centrifuged at high speed, and the milk solids allowed to freeze on to a refrigerated disc after being blown from the ice by means of a steam jet. The frozen milk solids are scraped off the revolving disc in the form of flakes which are dried in a vacuum at moderate heat.

Drying by means of cold and sublimation under vacuum has not yet reached commercial status on a large scale, principally due to the difficulty in removing the huge volume of water vapour created. A full description of the process is given in Hunziker's book.

**Dough Drying.**—In this method, now mainly out of use, the dough from the condensed milk kettle, when nearly all the water had been removed, was spread out into a band and dried by means of loss of heat.

**Film Drying.**—The milk is applied in a thin film to the surface of a rotating steam heated metal drum. The film of dried milk is continuously

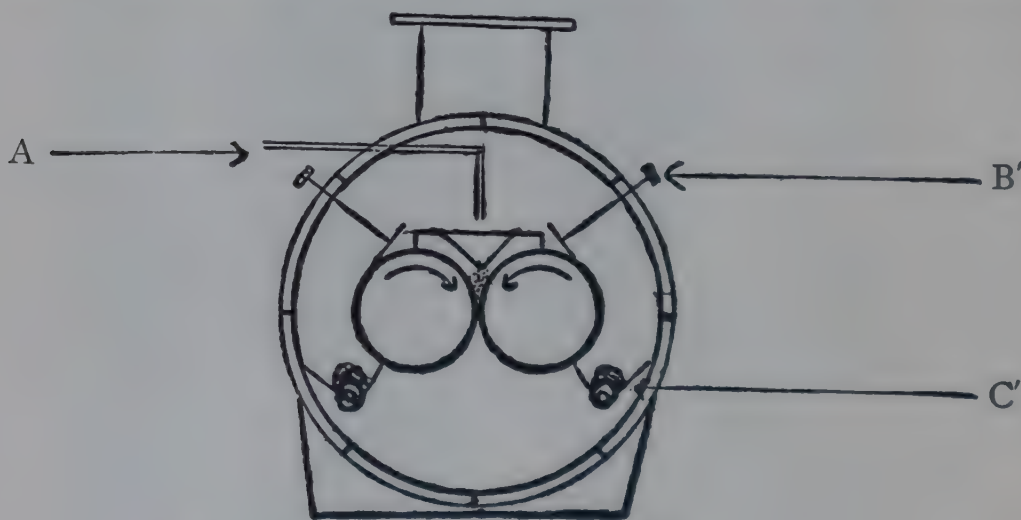


FIG. 23.—A Double Drum Vacuum Drier.

scraped off by a stationary knife located opposite the point of application of the milk. This constitutes a very simple method of drying milk, but the flavour of the milk is often spoiled somewhat by the high temperature used, especially when the scraper does not remove all the dried milk from the drum, and the dried milk is in contact with the hot drum for more than one revolution.

The solubility of drum dried milk is improved by homogenising before drying.

Milk for human consumption is more palatable when vacuum drum dried. The milk is of better keeping quality than atmospheric drum dried milk. The initial layout is more expensive, as is the operating cost of the vacuum drum drier. One of the latest designs of vacuum drum drier is shown in the diagram. The milk is precondensed to a high ratio (about 4 : 1) and fed into the drier by the pendulum feed A which distributes the viscous milk over the trough feeding the rollers. This precondensation is necessary because of the slower operation of a vacuum drier in producing milk of higher quality at lower temperatures. The



knives B, B' drop the dried milk into the screw conveyors C, C' which transfer the dried milk into a compartment (not shown) which may be emptied without breaking the vacuum.

The relative rapidity of the evaporation (the short heat exposure), and the low temperature used in conjunction with the vacuum, enables a high quality of milk to be made with very slight damage to the protein and consequent good taste. The solubility of this type of dried milk is also relatively high.

**Flake Drying.**—Borden method. Briefly, this method comprises a wire mesh band which is drawn through a foam made from precondensed milk and air. The evaporation takes place from this mesh as it passes through an air-heated tunnel. The dried flake is removed from the mesh by means of mechanical fingers. Because of its porosity this product dissolves rapidly and has good solubility again because of absence of contact with heated metallic surfaces. One disadvantage, however, is the large quantity of air incorporated in the foam. This causes some oxidation of the fat with consequent rancid flavour. Because of this disadvantage, the Borden method is only used for drying skim milk of low butterfat content. High quality skim milk is produced by this method.

**Spray Drying of Milk.**—The basic principle of spray drying milk is to reduce the milk to an "atomised" mist in the presence of a current of heated air. The atomised mist offers a huge surface for evaporation, and the milk is powdered before it falls to the floor of the evaporator. The idea of spray drying did not develop in the milk drying industry. It was conceived by Samuel Peray of New York, who patented the idea in 1872. Since these days the technique has been vastly improved. The Scott spray drier will be described here as an example of the equipment which has been perfected recently.

Fig. 24 shows the layout of the Scott spray drier.

Filtered air is sucked into the drier at A and heated by B. From here the air passes into the large chamber over the hot air diffuser C. The preconcentrated milk enters the drier via the tube E and is atomised by the rotary atomiser D revolving at 6,000 revolutions per minute. The rotary powder dischargers are shown at F. These clear the floor of the drier and transfer the powder to the powder conveyor and discharge lock G. The textile filter H removes the remaining powder from the air-flow. J is the exhaust fan which causes the air-flow.

The heart of the spray drier is the atomiser, and in the Scott spray drier this is of the stream-lined rotary type, impeller-shaped with wide non-choking passages. It rotates at 6,000–12,000 r.p.m. with direct electric drive by a special high speed motor.

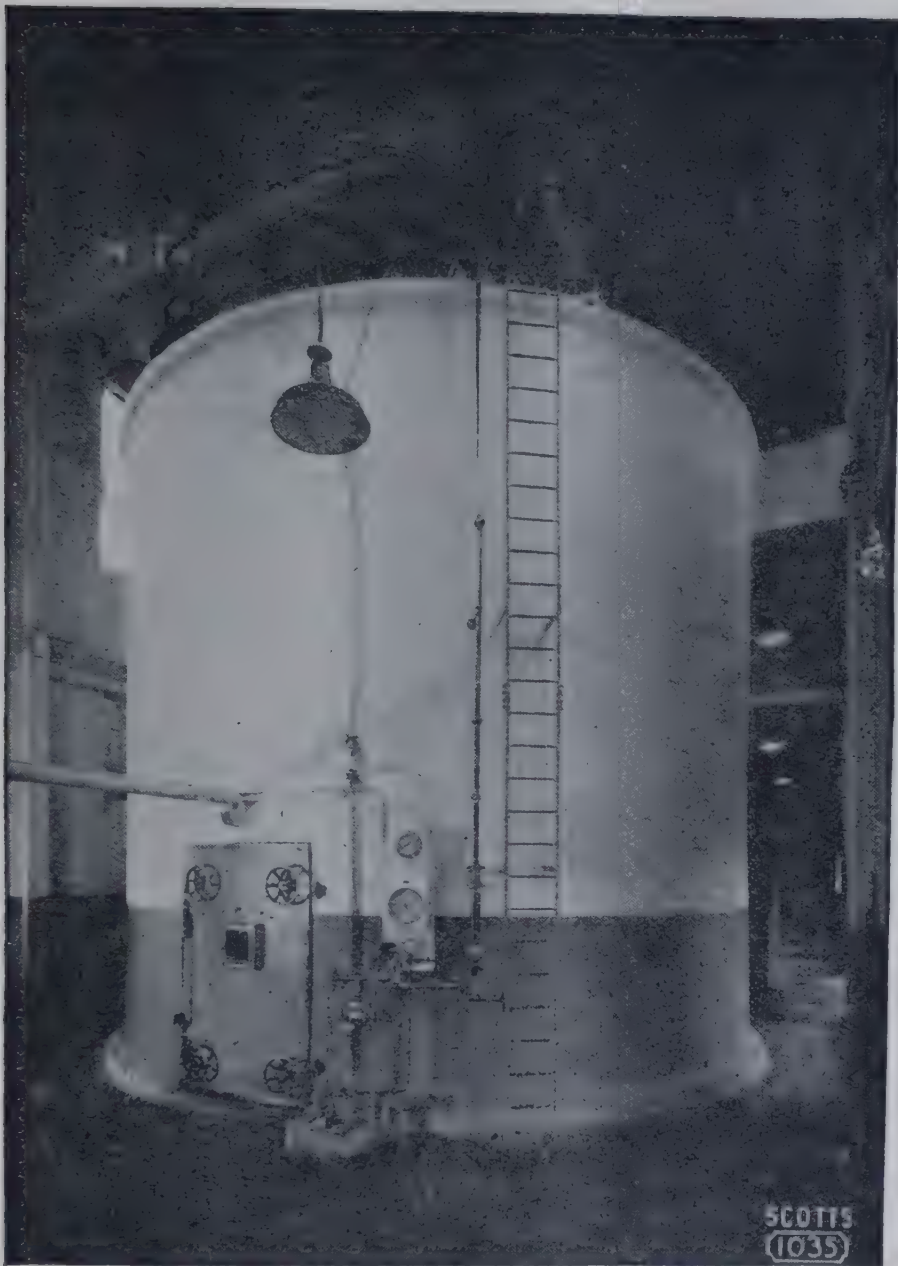
The liquid, after preconcentration to, say, 55 per cent., to be dried is pumped under pressure to the drying chamber and flows freely into the atomiser where it is subjected to centrifugal force and broken into a spray of extremely fine drops. These are thrown horizontally from the atomiser, forming a flat umbrella spray.

The drying medium of warm air is drawn through the whole installation by a fan arranged at the exhaust. The temperature of the drying chamber is between 130° F. and 175° F., corresponding to an adiabatic saturation point of 95° F.

Owing to the enormous surface produced by fine atomisation, the moisture contained in the tiny particles is instantly absorbed by the drying air. The spray is thus transformed into a fine dry powder before coming in contact with the walls of the chamber. Most of the powder drops to the bottom of the chamber. Part of the material, however, is entrained by the air which is passed through a filter in which all the powder is recovered. The powder recovered from the filter is automatically returned to main discharge. From the bottom of the drying chamber all powder is continuously collected by rotating scrapers and discharged at one point. All parts of the drying chamber are well illuminated so that the







*By courtesy]*

*[Messrs Geo. Scott & Son Ltd., London and Leven.*

FIG. 25.—A large Spray Drier.

performance and quality of the product can easily be supervised from the control panel. Fig. 25 shows a photograph of one of the largest units yet built.

Major advantages of this method of milk drying are:—

- (1) Low steam requirements—8 lbs. steam for 10 lbs. of milk.
- (2) Large capacity—15,000 lbs. of milk per hour.
- (3) A highly soluble powder is produced—99.8 per cent.

If maximum thermal economy is required, high preconcentration should be carried out.

Milk powders contain from 2–7 per cent. moisture. Typical milk powder compositions are:—

	Dried Whole Milk.	Dried Skim Milk.	Whole Milk.
Water . . . .	2.00	3.23	87.8
Fat . . . .	27.00	0.88	3.4
Proteins . . . .	26.50	36.89	3.4
Milk sugar (lactose). .	38.00	50.52	4.7
Ash . . . .	6.05	8.15	0.7
Lactic acid . . . .	...	1.40	...
Total .	99.55 *	101.07 *	100.0

\* Sum-total of analytical errors.

For statistics as to imports and exports of condensed and dried milk see Appendix III.



## VIII.—MARGARINE MANUFACTURE

By G. MARTIN, Ph.D., D.Sc.

### LITERATURE

Most of the facts in the accompanying article were supplied privately by firms interested in the manufacture of margarine. Much of the published literature is very poor, and often describes methods in vogue over twenty years ago and now abandoned.

G. HEFTER.—“*Technologie der Fette u. Öle*,” vol. iii. Berlin, 1910. Gives the best account.

LEWKOWITSCH.—“*Oils, Fats, and Waxes*,” vol. iii. (1901 edition).

Dr K. WINDISCH.—“*Margarinekäse*.” Berlin, 1898.

“*Die Margarine-Fabrikation*,” von TH. BUDDINGER. Separat-Abdruck aus dem Organ für den Oel- und Fetthandel. 2nd Edition. “Verlag. N. Besselich.” Pp. 16. Trier, 1910.

### ARTIFICIAL BUTTER, MARGARINE

Butter fat is a mixture of the glycerides (both simple triglycerides and mixed glycerides) of acetic, butyric, caproic, caprylic, lauric, myristic, palmitic, stearic, arachidic, and oleic acids. It also contains small amounts of cholesterol and natural colouring matters (lactochromes). The average proportions of the acids are as follows: Stearic acid, 0.49 per cent.; palmitic acid, 18.23 per cent.; myristic acid, 11.08 per cent.; lauric acid, 16.4 per cent.; oleic acid, 36.1 per cent.; caproic, caprylic, and capric acids, 3.23 per cent.; butyric acid, 6.13 per cent.; glycerol, 12.5 per cent. Cow butter consists of fat, 83.91 per cent.; water, 7.5-13.75 per cent.; casein, 0.5 per cent.; milk sugar, 0.3 per cent.; ash, 0.3 per cent.; salt, 1.2 per cent.

Since glycerides of the same fatty acids are present in varying amounts in many other fats and fatty oils, the problem which confronts the margarine manufacturer is the blending together of these fats so as to produce a substance having the same chemical composition as butter. Chemically this could be done by separating pure glycerides from the various fats (making them artificially if necessary) and then blending them together in the exact proportions in which they occur in butter fat. On the large scale this operation is quite impracticable on account of cost, so that the art of the margarine manufacturer consists in utilising the fats ready to hand, and blending them together in such proportions as most closely simulates the natural product. This has been so successfully achieved that many of the margarines now on the market resemble butter so closely in physical and chemical properties that the analyst has often very great difficulty in deciding whether a sample consists of true or artificial butter. There can be little doubt that ultimately a margarine will be produced having almost exactly the same constituents as natural butter, and therefore indistinguishable from it either by chemical tests or natural flavour.

### Manufacture of Margarine

The following ingredients are used in various percentages according to the quality of the margarine it is desired to produce: oleo oil, neutral lard, cocoa-nut oil, earth-nut oil, sesame oil, and cotton-seed oil. The refining of oils has become so perfect of late, through the application of the so-called American “Wesson Process,” that the oils used are now absolutely flavourless and neutral. About 50 per cent. of carefully soured cream or milk is churned through the above-named fats, and these, being quite tasteless, adopt the milky and buttery flavour of the soured cream. To the highest grades up to 10 per cent. of pure butter fat (the



highest percentage allowed by law) is still added, which brings the quality so near the real article that even experts often cannot detect any difference.

All countries nowadays make about the same blends. Generally speaking, one can say that higher grades contain about 10 per cent. of oil, 70 per cent. of oleo oil, and 20 per cent. of cocoa-nut oil, whilst lower grades contain up to half oil and half animal fats.

**Process of Manufacture.**—The milk, after a searching bacteriological and qualitative examination, is passed through the separators where the cream is separated from the milk. The cream is either churned into butter, or, what is usually more profitable, sold as cream. The separated milk is at once pasteurised (*i.e.*, heated to a temperature a little below its boiling point in order to destroy bacteria) and immediately cooled to nearly freezing point, remaining at this temperature until required for the “souring tanks,” when it is again warmed to a moderate temperature suitable for the souring culture which is then added. The souring culture is prepared in the bacteriological laboratory in the most careful manner, since the buttery flavour of the whole yield of margarine is dependent upon this. The milk is then allowed to “ripen” in a series of great open tanks, in which the milk is gently worked to and fro during the process; the floor is of concrete, and clean water is kept flowing over it, while the walls of the room are of glazed white ware, so that at this stage the danger of introducing foreign bacteria is minimised.

The milk thus prepared is now mixed in suitable quantities with the above-mentioned animal and vegetable oils in suitable proportions, and the mixture is thoroughly churned for not more than one hour in a suitable machine. The temperatures vary from 20°-45° C. The higher the quality the lower the churning temperature, the object being to retain as much as possible of the delicate milk flavour, which a high temperature largely destroys. In this way the product gets the characteristic smell and taste of butter.

Then, the property of butter to brown and froth being due to casein and milk-sugar, suitable proportions of these, or sometimes also of “Elaine,” extracted from yoke of eggs, are added to high grade margarines.

In the churning machines the ingredients are thoroughly beaten into an emulsion or cream, the mixture being pulverised into single globules such as butter fat forms in milk, the process being regulated if necessary by means of steam or ice water sent through the steam jacket with which the churn is provided. The mass is then run out into large wooden tanks (sometimes coated with marble slabs, cleanliness being everywhere of the utmost importance). While running out in a thin stream from the churns the fluid margarine is met by a high-pressure jet of cold water, which pulverises the margarine, so that the disintegrated globules after solidifying resemble butter granules very closely.

This method of chilling the margarine has always been a source of dissatisfaction to the manufacturer, as it is impossible to perfectly control it, and even under the most favourable circumstances it did not give the best results for the following reasons:—

1. The milk serum in the emulsion is partly replaced by water.
2. Part of the souring culture is washed out, this resulting in an irregular and insufficient development of the souring ferment during the subsequent operations.
3. The chilling not being carried out at a sufficiently low temperature, the finished margarine is always of a softer and more greasy texture than butter.

To remedy these defects a process has recently been patented by Mr E. Schou which does away with the water cooling. The emulsion as it leaves the churn is spread out into very thin layers of about one-fiftieth of an inch in thickness on two large drums, revolving at the same speed but in opposite directions. These drums are cooled down by means of refrigerated brine to a temperature of about -10° C., so that the very thin layers of emulsion immediately crystallise on the drums, and while retaining the whole of the milk serum, are scraped off in thin flakes, and treated as subsequently described. The advantages of this method are very great, viz. :—

1. The whole of the milk serum and souring culture being retained, a perfect control of the flavour of the margarine is secured.
2. Through the more effective cooling, the texture of the margarine becomes firm and at the same time pliable, and both to the naked eye and under the microscope it is hardly to be distinguished from butter.



The process has been worked for some time by one of the largest firms of margarine manufacturers in this country with such success that the best qualities of margarine thus prepared are equal, if not superior, to the best qualities of pure butter.

The solidified margarine is now removed in wooden waggon to the fermenting rooms, where the excess of water is allowed to drain off, and the souring culture in the milk allowed to develop and flavour the whole mass of margarine. After "ripening" for a sufficient time, the mass is transferred to large kneading machines in order to squeeze out the excess of water and obtain a homogeneous mass. Salt may here be kneaded in to taste, together with colouring matter to produce the fine yellow colour characteristic of butter. Many colouring substances are sold (some even being aniline dyes).

Two harmless colouring mixtures much used are these :—

(a) Orlean, 80 parts ; curcuma root (turmeric), 80 ; olive oil, 240 by weight ; saffron, 1 part mixed with alcohol, 5 parts by weight. Macerate the orlean and turmeric with olive oil, express, make up the weight of the filtered liquid to 240 parts by weight with olive oil ; then add the filtered saffron-alcohol extract, stir, and expel the alcohol by heating the mixture.

(b) Moisten 30 parts of finely powdered alum with 3 parts of turmeric extract, spread out and dry the powder in a warm place ; then pulverise finely, and store, protecting the product from the light. A pinch of the powder added to a churnful of milk or cream before the churning imparts a beautiful golden colour. The turmeric extract is made by adding 1 part powdered turmeric to 5 parts alcohol, and macerating together for about a week ; then filtering. After the kneading the margarine is moulded into lumps, pats, etc., ready for the market.

As a food margarine is little (if at all) inferior to butter, and being prepared from the freshest and purest materials, is usually cleaner than butter as prepared in the dairy.

**Distinctive Tests between Butter and Margarine** (see also pp. 64, 75).—1. The Reichert-Meissl value (see under Fat Analysis) for butter is very large (20-33 cm.). That of most fats range from 0.5-1.5 cm. (cocoa oil, 7-8). Margarine makers now often add glycerides of volatile acids, so as to obtain the same number as with true butter.

2. The saponification value of butter is high (221-233), that of other fats low. The addition of cocoa-nut oil to the margarine raises its saponification value to that of butter.

3. The refractive index of butter is 1.4590-1.4620 at 25° C. (butyro-refractometer scales, 49.5-54). That of margarine is 1.4650-1.4700 (58.6-66.4 butyro-refractometer divisions). Cocoa-nut oil lowers the refractive index of margarine to that of butter.

4. True butter fat contains less than 1 per cent. of stearic acid. Most margarines contain 10-20 per cent., and even more. For other tests see under Butter.

S. H. Blichfeldt (*Jour. Soc. Chem. Industry*, 15th July 1910, p. 792, vol. xxix.) has devised a process for the estimation of butter and cocoa-nut fat in margarine.

The fat is saponified by a mixture of aqueous potash and glycerol, and the fatty acids are liberated by acidification with sulphuric acid. The resulting mixture is distilled in a specially designed apparatus, made by Becker, London.

The distillate is treated with an excess of decinormal soda solution and transferred to a 200 c.c. measuring flask. The total volatile acids are determined by titrating back with decinormal sulphuric acid. The neutral soap solution is now treated with excess of decinormal silver nitrate solution, and 10 per cent. of solid sodium nitrate is dissolved in the liquid in order to salt out all the sparingly soluble silver salts. After making up to 200 c.c., the precipitated silver salts are filtered off, and the excess of silver nitrate is determined volumetrically in the filtrate. The volatile fatty acids are thus determined as soluble and insoluble silver salts.

The ratios of soluble to insoluble silver salts, derived from butter and cocoa-nut fats respectively, differ considerably from one another, and afford a ready means of determining these substances in presence of one another.

**Suet substitutes** consist of a mixture of suet (tallow) and cotton-seed oil or cotton-seed stearin.

**Lard substitutes** are mixtures of lard or "lard stearine" (p. 26), with cotton-seed stearine, maize oil, cocoa-nut oil, and other similar oils. In Germany such substitutes are heated with onions and condiments, and sold as cooking fat (*bratenfett*).

**Margarine Cheese** is made from milk from which the cream has been removed, and to which margarine fat has been added. Otherwise the operation is just like cheese-making in the ordinary way (see under Cheese). In 1910 about 1,600 cwt. (value, £2,500) were imported into Great Britain.

**Statistics.**—The amount of margarine imported into the United Kingdom is given by the following figures:—

	1906.	1910.	Value in 1910.
	Cwt.	Cwt.	
Margarine - - - -	1,101,900	1,120,800	£2,900,000
„ cheese - - -	1,200	1,600	2,500
Imitation lard - - -	231,000	275,000	600,000

Exported was 7,000 cwt. (value £17,000), in 1910, of margarine; and 2,700 cwt. (value £6,600) of imitation lard.

The United States in 1910 exported 74,556,000 lbs. of lard substitutes (value, \$6,887,000), and 3,418,000 lbs. of oleo-margarine or imitation butter (value, \$350,000).

For modern statistics see Appendix III.

See also chapter on the Hardening of Fats. Hardened fats are now used in a very pure form for the manufacture of margarine.

The author thanks Mr Paul Arup for much information regarding the modern raw materials used in the manufacture of margarine.



## IX.—THE FATTY ACID INDUSTRY

BY I. McARTHUR.

### LITERATURE

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The naturally occurring fatty acids are, in general, straight chain aliphatic substances, having from four to thirty or more carbon atoms in the molecule, and they form in combination with glycerol the oils and fats which are synthesised by vital processes in plant and animal tissues. Plant and animal waxes are formed from fatty acids in combination with fatty alcohols. The fatty acid industry is concerned with the breaking down of these natural products and the recovery and refining of the constituents.

In any oil or fat there is a number of different fatty acids present, the proportions and types being roughly characteristic of the source. There are two main types of acids, those which are solid at normal atmospheric temperature, and those which are liquid. The solid acids exhibit a crystalline structure, and the manufacturer can effect a fairly complete separation of solid from liquid by processes involving crystallisation, pressing and filtering. The employment of inert solvents as diluents can materially assist in these processes. A certain measure of separation can also be achieved by fractional distillation as the boiling-points of acids increase with the number of carbon atoms present in the molecule. In general, the fatty acids handled in the industry range from those with 10 carbon atoms to those with 22 carbon atoms in the molecule.

Where a preponderance of any particular fatty acid is required it is possible to select an oil or fat of known composition for its preparation. Economic consideration, however, and the availability of supplies, usually restrict the raw materials used in the industry to a rather narrow range.

The demand for fatty acids falls into three sections depending on the purposes for which they are required. Some uses call for predominantly solid fatty acids or stearine, consisting largely of a mixture of palmitic and stearic acids with only small proportions of oleic and other liquid acids. Other uses call for liquid fatty acids or oleines with a minimum content of solid acids. These two types are commonly prepared by the pressing and filtration methods mentioned above. Certain uses, however, require specialised properties, and these are met by selection of the most suitable raw oil from which the fatty acids are either refined by direct distillation or further separated by fractional distillation.

**Raw Materials.**—The main use for animal and vegetable oils and fats is for edible purposes, and for these they must be refined. The acid oil by-products from bleaching and neutralising find use in soap making and fatty acid manufacture. The next demand, in order of size, is for soap making purposes and here good coloured oils and fats are required. Dark coloured material, fats recovered from residues, refinery by-products, and off-quality or crude oils are the main raw materials for the fatty acids industry.

Of these the most important is bone grease, the fat recovered from bones in



the process of rendering them down to glue and bone meal. Bones recovered from the slaughterhouses and butchers are boiled with water under pressure and the fat which is released is separated from the water. A better yield of fat, though of a rather lower grade, is obtained when the bones are crushed and extracted with petroleum solvent or benzine, the solvent being subsequently removed by distillation. Skins and offal are similarly treated to yield skin grease and gut grease. The lower qualities of tallow, recovered by steam rendering the fatty tissues of beef and mutton, are also much used.

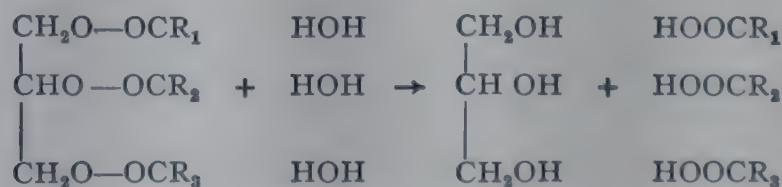
Amongst vegetable oils and fats palm oil, obtained from the fleshy covering of the fruit of the West African oil palm, is extensively used in the production of stearines, and the lower grades of the palm kernel oil obtained from the same tree find use in the preparation of specialised fatty acids owing to the large content of low molecular weight acids. Coconut oil obtained from copra, the dried flesh of the coconut, is also a source of the lower fatty acids.

Chinese vegetable tallow is remarkable for its high content of palmitic acid, and shea butter for its high content of stearic acid. Liquid acids are predominant in groundnut oil, and rape oil contains a solid unsaturated acid, erucic acid with 22 carbon atoms. Castor oil contains mainly ricinoleic acid, a fatty acid which, having a hydroxyl group in the chain, has rather specialised properties. Cotton-seed oil contains mainly palmitic and liquid acids; kapok, maize and sunflower seed oils have relatively small proportions of solid acids, but the liquid acids are rich in linoleic acid. Soya bean and linseed oils contain larger proportions of linoleic acid, and also linolenic acid which gives them the property of drying on exposure to air to the tough films required in preparation of paints.

Owing to the quantity of whale oil refined for edible purposes, the lower grades and the by-products acid oil are used as a source of cheap fatty acids, but the presence of highly unsaturated acids prevents their use in the production of high grade oleine. Fish oils obtained from herring, sardine and menhaden, containing larger proportions of highly unsaturated acids, yield products suitable for use in preparation of paints.

The most commonly used waxes, in which fatty acids are combined with fatty alcohols instead of glycerine, are wool fat and sperm oil. Wool fat, recovered from waste wash waters in the woollen industry, contains, in addition to fatty acids derived from the soaps and wool lubricants used, the wax found on the raw wool fibres. This consists of fatty acids in combination with cholesterol and other cyclic alcohols. Sperm oil obtained from the head cavity and blubber of the sperm whale consists of fatty acids combined with straight chain fatty alcohols of similar chain length.

**Types and Properties of Fatty Acids.**—Fats and oils are triglycerides of mixed fatty acids where two or three different acids may be combined with one glycerine molecule. They are saponified or split by hydrolysis in the following manner:—



1 molecule fat + 3 molecules water  $\rightarrow$  1 molecule glycerine + 3 molecules fatty acid.

$R_1, R_2, R_3$  represent different fatty acid radicals of the form  $\text{CH}_3(\text{CH}_2)_n$  which are attached to the active carboxyl group  $\text{—COOH}$ .

Molecules in which each carbon atom is attached by a single bond to the next are described as saturated. In practically all naturally occurring fatty acids  $n$  is an even number, and the lower members of the series where  $n$  is small are liquids. As the number of  $\text{CH}_2$  groups in the chain increases the melting-point rises.



	M. Pt.	Mol. Weight.
Caprylic acid, $\text{CH}_3(\text{CH}_2)_6\text{COOH}$ .	16° C.	144
Myristic acid, $\text{CH}_3(\text{CH}_2)_{12}\text{COOH}$ .	54° C.	228
Stearic acid, $\text{CH}_3(\text{CH}_2)_{16}\text{COOH}$ .	70° C.	284

Molecules in which two or more carbon atoms are attached by double bonds are described as unsaturated, and the melting-points are lower than those of the saturated acids of the same chain length. Oleic acid, which is the most commonly occurring of fatty acids, has one double bond. Linoleic acid of the same chain length has two, and linolenic acid three double bonds. The presence in the chain of other groups, such as the hydroxyl  $\text{—OH}$  in ricinoleic acid, also lowers the melting-point.

	M.-Pt.	Mol. Weight.
Myristoleic acid, $\text{CH}_3(\text{CH}_2)_3\text{CH}=\text{CH}(\text{CH}_2)_7\text{COOH}$ . . .	Liquid	226
Oleic acid, $\text{CH}_3(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_7\text{COOH}$ . . .	16° C.	282
Linoleic acid, $\text{CH}_3(\text{CH}_2)_4\text{CH}=\text{CH}\text{CH}_2\text{CH}=\text{CH}(\text{CH}_2)_7\text{COOH}$ .	-5° C.	280
Linolenic acid, $\text{CH}_3(\text{CH}_2)\text{CH}=\text{CH}\text{CH}_2\text{CH}=\text{CH}\text{CH}_2\text{CH}=\text{CH}(\text{CH}_2)_7\text{COOH}$	-11° C.	278
Ricinoleic acid, $\text{CH}_3(\text{CH}_2)_5\underset{\text{OH}}{\text{CH}}\text{CH}_2\text{CH}=\text{CH}(\text{CH}_2)_7\text{COOH}$ . .	5° C.	298

The reactivity of fatty acids depends on the terminal carboxyl group and on the double bonds. The carboxyl group reacts with alkalis to form soaps; from these the alkaline radical can be substituted with others, such as calcium or copper, to form insoluble stearates and oleates.

Fatty acids react with ammonia under pressure to form amides  $\text{R.CONH}_2$ , which, under high temperature, can be dehydrated to yield nitriles  $\text{R.CN}$ . These on hydrogenation are converted to amines  $\text{R.CH}_2\text{NH}_2$ .

Acid chlorides are prepared by reacting fatty acids with phosphorus pentachloride, and these form intermediates for other derivatives. Esters may be prepared by heating fatty acids with alcohols of different type. In this way edible fats are reconstituted by the use of glycerine, and drying oils for the paint trade by the use of glycerine or pentaerythritol.

The double bonds in unsaturated fatty acids can take up hydrogen in the presence of suitable catalysts to form the corresponding saturated acids. This is the basis of the extensive fat hardening processes used in production of edible fats from whale oil (see pp. 100a-100p).

Sulphuric acid is added on at the double bond when unsaturated fatty acids are treated with oleum or fuming sulphuric acid to yield sulphuric esters which, when neutralised with alkali, form the "sulphonated" oils used as wetting agents. (See under Soapless Detergents.)

The double bond will absorb oxygen from the air, giving rise to rancidity or, in the case of fatty acids with two or more double bonds, leading to oxidation and fusion of two or more molecules to give the polymers which are the basis of paint films.



## MANUFACTURE

## Cleansing

In the manufacture of fatty acids the first step is normally a preliminary refining of the low grade fats to render them suitable for splitting. This may be either a boil with dilute sulphuric acid to separate emulsions and remove any water soluble impurities, or by heating with strong sulphuric acid in lead-lined vessels to char out non-fatty and albuminous matter. In some cases the fat is merely mixed at elevated temperatures with acid bleaching earth and filtered.

## Splitting

Since the foundation of the industry in 1825, following on Chevreul's research on the nature of fats, various methods have been adopted for splitting.

**Saponification.**—Fats heated with caustic alkalis are converted to soap and glycerine, the soaps being afterwards decomposed by boiling with dilute acid to liberate the fatty acids.

**Enzyme Splitting.**—An enzyme preparation obtained by fermenting a mash of castor beans, when emulsified with fats under carefully controlled conditions, will split them in a period of 24–48 hours.

**Acid Hydrolysis.**—Fats heated to 120° C. and mixed with 4–6 per cent. of strong sulphuric acid are sulphonated. On prolonged boiling of the mass with water, fatty acids are liberated. This process was of considerable importance to the candle industry, as liquid unsaturated acids were partly converted to solid hydroxy acids, but much of the glycerine was lost. Only two methods are now in general use: Twitchell splitting, and the Autoclave process with its more recent development of high pressure splitting.

**Twitchell Splitting.**—Twitchell reagent is a sulphonated emulsifier. Based originally on the sulphonated product of a mixture of oleic acid and naphthalene, many different compositions have proved satisfactory. The type most used now is prepared by sulphonation of naphthenic acids obtained as a by-product of the refining of mineral oils.

Precleansed fat is boiled by means of open steam with 20–50 per cent. of its weight of water, containing 1 per cent. sulphuric acid and about 1 per cent. of Twitchell reagent. The fat charge may be from 5 to 30 tons, and boiling is carried out in wooden tubs or in iron tanks lined with lead or corrosion-resistant alloy. Splitting is rapid with a clean fat, but the reaction is reversible, and hydrolysis will only proceed to a stage determined by the concentration of the separated glycerine in the water. At this stage steam is shut off and the charge separates into two layers. The sweet water is drawn off the bottom and a fresh charge of water and acid added. It is usual to carry out the reaction in three stages to obtain a split of 95–98 per cent. free fatty acids, each stage occupying from 5 to 10 hours.

The separated sweet water, which contains about 10 per cent. glycerine, is treated with lime or barium carbonate to remove the sulphuric acid and any water-soluble fatty acids before evaporation to recover the glycerine. The quality of the crude glycerine is dependent on the nature of the raw fats and the treatment given to the sweet water, but, in general, a single distillation will yield dynamite quality glycerine.

Twitchell splitting requires only simple plant and it can be readily controlled to give satisfactory results even from low grade fats. The fatty acids produced are, however, invariably dark in colour and for most purposes require subsequent distillation to improve the appearance.

**Autoclave Process.**—Oils and fats can be split to an extent by the action of hot water. This process is catalysed by the use of small amounts of zinc,



magnesium, or calcium oxides, and proceeds more quickly at increased temperatures. Autoclaving, operated as a batch process, is one of the earliest commercial methods of fat splitting. It is best applied to good quality or well cleansed fats, and has the advantage that the fatty acids produced are not so dark in colour as those from Twitchell splitting.

A charge, which may be up to 5 tons, is taken in a vertical cylindrical autoclave with dished ends, constructed of copper or corrosion-resistant steel, and 10 per cent. of water containing catalyst equal usually to 1 per cent. on the fat is added. The vessel is closed and heated with open steam at 100–160 lbs. pressure to a temperature of 170°–190° C. for 4–5 hours. The charge is stirred mechanically or by allowing a small leak of steam from the vessel. The splitting reaction is reversible, and is best carried out in two or three stages. At the end of the first stage the sweet water is blown out from the bottom, and a fresh charge of 15 per cent. of water pumped in for the second stage. Condensation of steam brings the sweet water up to about 25 per cent. on the charge for each stage, and the total time under pressure is from 7–12 hours to reach a split of 95–98 per cent. free fatty acids. At the end of the process the fatty acids, containing soaps formed with the catalyst, are washed to free them from any entrained glycerine, and the soaps decomposed by boiling with dilute sulphuric acid.

**High Pressure Splitting.**—With the introduction of corrosion-resistant steels it has been possible to construct plant capable of withstanding the attack of fatty acids at high temperature and pressures. Processes have been developed for the continuous counter current splitting of fats by water without the need for added catalyst, which show considerable advantages in operating cost when a uniform feed stock of good quality fat is available. In these, water and fat are preheated to the reaction temperature of 240°–260° C. and pumped at pressures of 600 lbs. or over through a vertical stainless steel autoclave which may be up to 70 ft. high. The water is introduced near the top and percolates downwards through the fat, which is introduced near the bottom, progressively splitting it and removing the glycerine. Sweet water is continuously removed at the bottom and flashed into a separator tank, from which unevaporated liquid is passed direct to the evaporator to recover the glycerine.

Fatty acids are taken off continuously at the top above the entry point of the water. Conditions and quantities of water and fat are so adjusted that fatty acids are taken from the column at 98 per cent. split and sweet water at a content of 15 per cent. or more of glycerine.

### Refining

Fatty acids are refined by distillation and, as they tend to decompose at their boiling-point, it is necessary to distil either in steam or under vacuum.

**Steam Distillation** in batch stills is carried out in much the same way as was practised in 1850, except that stainless steel is replacing the cast iron and copper originally used for the construction of the stills.

A charge of 6–9 tons is taken through main (A) (Fig. 26) into a cylindrical dish ended still (B) set in brickwork. In this it is heated by direct firing from below (C), and by low pressure steam superheated to 320°–420° C. lead through perforated coils (D) into the fatty acids. The fatty acids distil over a range between 230°–300° C. at a rate regulated by the fire heat and steam flow, and are condensed in a series of vertical U-pipe air condensers (E), the distillate being led off through trap coils cooled in water jackets (F). The steam which passes through the air condenser is condensed by a water spray (G) on the last leg which is sealed by a water separator (H). The dark coloured residue in the still is discharged through a main (I) to a second still fitted with a bottom run off where steam distillation is continued at a higher temperature and some decomposition takes place. The residue which is finally run off the still is stearine pitch and amounts to 1–2 per cent. of the original fatty acids.

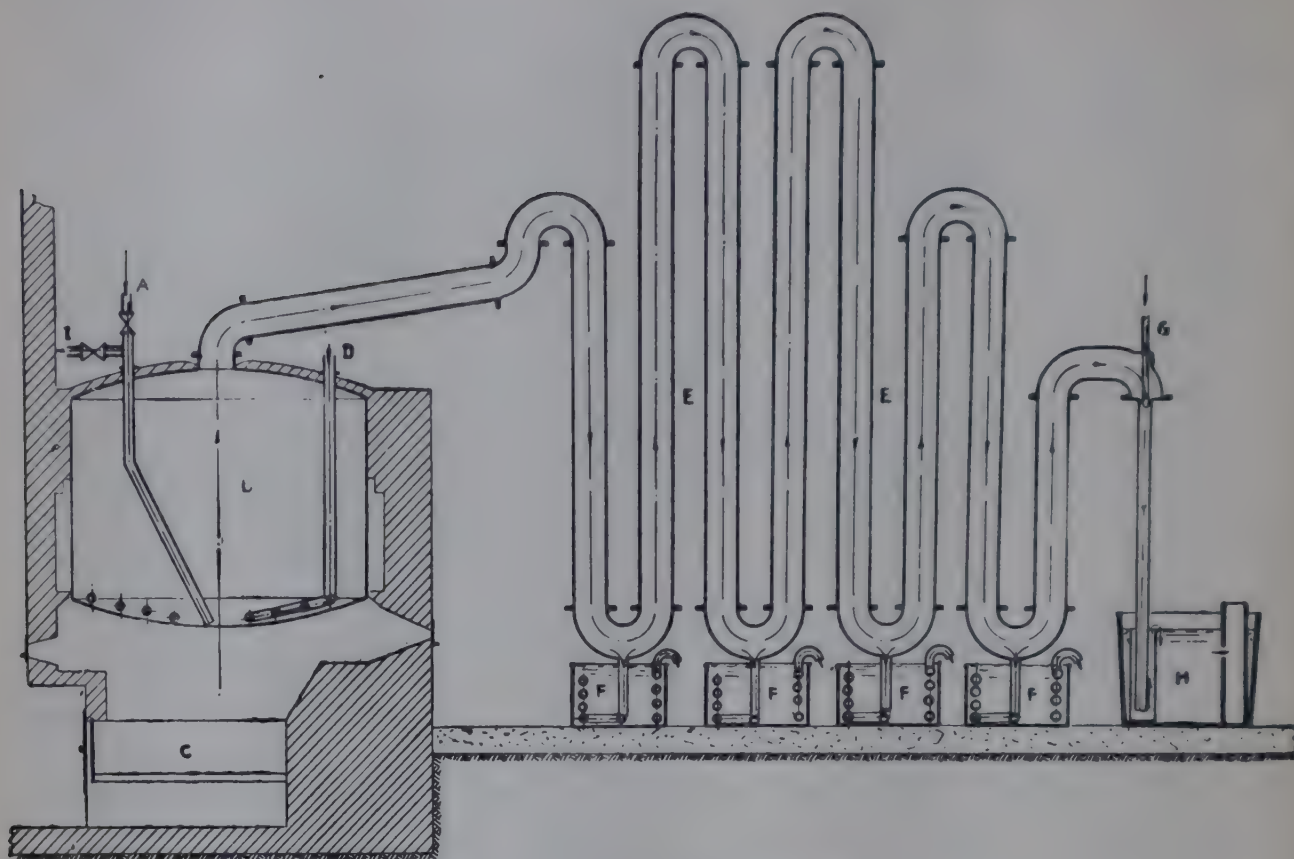


FIG. 26.—Steam Batch Still.

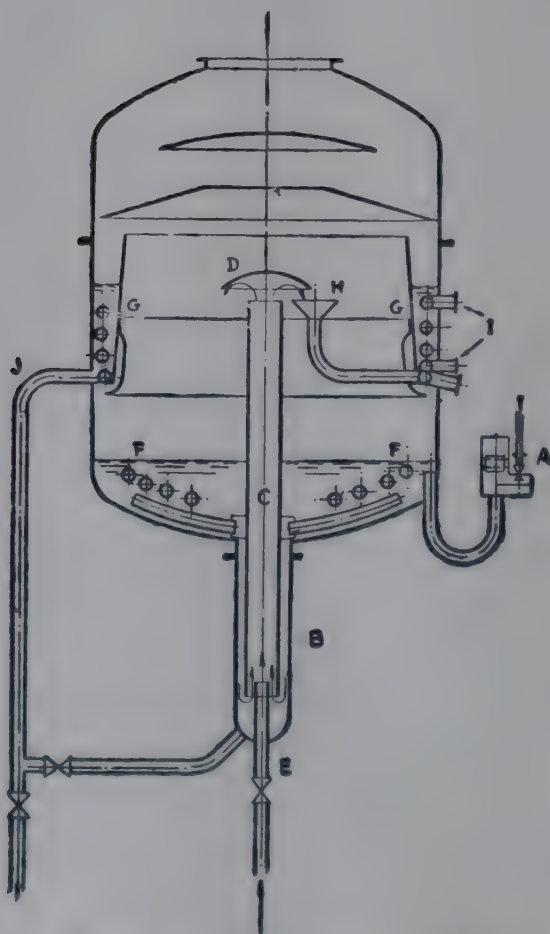


FIG. 27.—Lurgi Continuous Still.



**Vacuum Distillation** is now being more frequently used and there are many types of still designed for this purpose, both batch and continuous, some of which employ open steam to assist in vaporisation.

In the Lurgi continuous still (Fig. 27) fatty acid feed is taken through a preheater and a constant level device (A) to the still. This is a vertical cylindrical vessel of cast iron construction with a narrowed section (B) below, into which dips an open-ended circulating pipe (C), above which, in the body of the still, is a cup-shaped baffle (D). Fatty acids are forced by a steam jet (E) upwards through the pipe and strike the baffle which throws them downwards on to the closed steam heating coils (F) near the bottom of the still. On the wall of the still above the coils is a gallery (G) which receives through a wide scoop (H) a portion of the baffled spray. This gallery has a perforated steam coil (I) and a stop adjacent to the delivery from the scoop. Fatty acids collected here pass round the gallery to an outlet (J), being progressively distilled by the open steam so that the discharge is still residue amounting to about 10 per cent. on the charge. This is split again and redistilled. Fatty acid vapours taken from the top of the still are condensed in two vertical cylindrical condensers in series followed by a spray arrestor (not shown in diagram).

The still operates at a pressure of 3–5 m.m., developed by a series of steam ejectors and jet condensers, and is heated by steam at 45 atmospheres.

In the Scott continuous plant the stills are vertical cylindrical vessels of stainless steel, fitted with calandrias, heated by a diphenyl oxide system, through which the fatty acids are forced by centrifugal impellers. The feed is preheated at a pressure of 30 m.m. and drawn into the main still, which is at a pressure of 3 m.m. A continuous drain of material which has circulated the main still is run by gravity to a secondary still, operating under the same pressure but at a higher temperature, where the fatty acid content is reduced to about 30 per cent. Residue is withdrawn at intervals from the secondary still, to be resplit and redistilled. The distillates from the two stills are condensed in separate condensers fitted with calandrias cooled by water under pressure, which are in series with a third surface condenser cooled by water. Vacuum is maintained by a steam ejector and barometric condenser backed by a vacuum pump, and distillation is effected at 180°–220° C. without the need for open steam.

Vacuum distillation is also being applied on a commercial scale for separation of fatty acids. For this purpose fractionating columns of the type used in the lubricating oil industry, but constructed in stainless steel, are used. Owing to the small differences in boiling-points of acids of similar molecular weight, the separation is a difficult matter, and at best leads to a concentrate of certain acids stripped from selected stock in which the remaining acids are sufficiently dissimilar in nature to permit separation by this means.

### Separation

Fatty acids when cooled form crystalline solids. At atmospheric temperature liquid fatty acids can be separated from a crystalline cake of mixed fatty acids by pressure, and this constitutes the principal method for preparation of stearines and oleines.

Palmitic and stearic acids, the most commonly occurring solid acids in the fats and oils used in the industry, both form large crystals. Mixtures of the two acids, however, form crystals varying sharply in size with the proportions of each acid present. The addition of myristic and other solid acids will also markedly reduce the size of the crystals. To obtain a fatty acid cake with well formed crystals, from which the liquid acids will drain easily, it is necessary to select and blend the raw fats or the fatty acids to give a mixture containing solid acids in the correct proportion.

The blended fatty acids are filled when hot into shallow trays held in racks, where they are cooled slowly in air to allow crystals to grow. When crystallisa-



tion is complete the cakes are removed from the trays, slipped into pockets made of coir matting, and pressed at atmospheric temperature in hydraulic presses. The oil which separates is led away for further treatment, and the solid cake left in the pockets is shaken out and melted with open steam. At this stage it still contains about half the liquids originally present, and these are separated by further pressing. The melted cake is again blocked in trays cooled in air and pressed in pockets between steam-heated plattens in two stages, the cake being melted and reblocked before the final stage. The final cake, or stearine, is hard, white and crystalline and, dependent on the degree of pressing, may contain less than 2 per cent. of liquid acids.

The oil from the cold pressing is chilled slowly and filtered from the crystals that separate to yield liquid fatty acids or oleine. The oil from hot pressing is blocked and pressed in stages to yield a second grade stearine.

In order to avoid the heavy manual operations involved in pressing, the use of solvents has been introduced. In a suitable solvent it is possible to reach an equilibrium when the liquid fatty acids remain in solution while the solid fatty acids crystallise out. Much research has been done on this in the United States and the most promising results have been obtained with liquid propane and with methyl alcohol. The use of the latter has been developed into a commercial process by Emery Industries Inc., described in an article published in "Oil and Soap," vol. xxiii, for May 1946. In this process mixed distilled fatty acids are dissolved in 90 per cent. methanol at a solvent ratio of about 5 : 1 and cooled to 10° F. in a counter flow heat exchanging crystalliser. The cold slurry of solution and crystal is fed to a continuous rotary vacuum filter and the filtrate passed to a vacuum still for solvent removal. The crystalline cake is washed with solvent, melted, and distilled for solvent recovery. The products from tallow are stearine at 129½° F. titre and oleine at 30½° F. titre. Recovered solvent is returned to process and the flow of material so arranged that an efficient thermal balance is maintained.

### Uses of Fatty Acids

Fatty acids are essential raw materials for an increasing number of industries of which only the main uses can be mentioned here.

Stearines are used mainly in the preparation of cold process shaving soaps and creams, and in the manufacture of stearates. Calcium stearate is used as a modifier and lubricant for moulding in the plastics industry, and in metal stamping and wire drawing. Magnesium stearate is used very largely as a flattening agent in paints, and in lubricating oils as a thickener for grease manufacture. Aluminium stearate is used as a waterproofing agent both for textiles and in the building trade. The rubber industry uses stearine or fatty acids as a lubricant in reclaiming scrap. Furniture, floor, shoe and metal burnishing polishes are based on stearine as an emulsifying agent and binder. Stearates or fatty acids are used to replace the natural fats lost from leather during tanning. Cosmetic and pharmaceutical creams are based on stearine, which is also included in tooth paste and dentifrices. Textile finishes, glaze powders and sizes are prepared with stearine. In the dyestuffs industry stearine is compounded with the colours to enable them to be dispersed readily when used. Candle making, which was the original use for solid fatty acids, now takes only a small proportion of stearine owing to economic reasons.

The main use for oleines is in the textile industry. Wool is cleansed from its natural fat and dirt before processing and, to prevent fibre breakage and allow fine spinning, oleine is used as a lubricant. This is finally removed from the finished yarn or cloth by washing in alkali which combines with the oleine to form soap. Oleine is also used in the artificial silk industry to improve the handle and finish of the fibres. Soap making and laundry work absorb considerable quantities of oleine. Oleates are used in waterproofing, in paints, and as



plasticisers in cellulose base lacquers. Dry cleaners use oleine soaps in their solvents, and oleine itself enters into the preparation of stencils, carbon papers, and typewriter ribbons.

Mixed fatty acids are often used in place of oleine and stearine, an important use being the preparation of the mono and diglyceride esters used as emulsifiers in the food and textile industries. Many chemical derivatives of the fatty acids are the starting points for the manufacture of emulsifiers, detergents, froth flotation agents for mining, and insecticides.

Stearine pitch forms the basis of black stoving enamels and is also used as a sealing and insulating compound in the electrical industry, and for rubber compounding.

SATURATED FATTY ACIDS.  $C_nH_{2n}O_2$ .

Common Name.	Formula.	Mol. Wt.	M.-Pt. ° C.	B.-Pt. ° C.
Caproic . . .	$C_6H_{12}O_2$	116.15	- 3.4	205
Caprylic . . .	$C_8H_{16}O_2$	144.21	+ 16.7	237
Capric . . .	$C_{10}H_{20}O_2$	172.26	31.6	269
Lauric . . .	$C_{12}H_{24}O_2$	200.31	44.2	130/1 m.m.
Myristic . . .	$C_{14}H_{28}O_2$	228.36	53.9	150/ "
Palmitic . . .	$C_{16}H_{32}O_2$	256.42	63.1	166/ "
Stearic . . .	$C_{18}H_{36}O_2$	284.47	69.6	184/ "
Arachidic . . .	$C_{20}H_{40}O_2$	312.52	75.4	196/ "
Behenic . . .	$C_{22}H_{44}O_2$	340.57	79.9	..
Lignoceric . . .	$C_{24}H_{48}O_2$	368.62	84.2	..
Cerotic . . .	$C_{26}H_{52}O_2$	396.68	87.7	..
Montanic . . .	$C_{28}H_{56}O_2$	424.73	90.0	..
Melissic . . .	$C_{30}H_{60}O_2$	452.78	93.6	..

UNSATURATED FATTY ACIDS. MONOETHYLENIC.  $C_nH_{2n-2}O_2$ 

Lauroleic . . .	$C_{12}H_{22}O_2$	198.30	Liquid	130/ m.m.
Myristoleic . . .	$C_{14}H_{26}O_2$	226.35	"	155/ "
Palmitoleic . . .	$C_{16}H_{30}O_2$	254.40	- 1	165/ "
Oleic . . .	$C_{18}H_{34}O_2$	282.45	16.3	188/ "
Erucic . . .	$C_{22}H_{42}O_2$	338.56	33.5	..

## POLYETHYLENIC.

Linoleic . . .	$C_{18}H_{32}O_2$	280.44	- 5	..
Linolenic . . .	$C_{18}H_{30}O_2$	278.42	- 11	..
Clupanodonic . . .	$C_{22}H_{34}O_2$	330.49	Liquid	..

With the kind co-operation of Messrs Prices (Bromborough) Ltd.

## IXA.—THE MANUFACTURE OF CANDLES

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 MARAZZA—MANGOLD.—“Die Stearin industrie.” 1896.  
 F. MALEPEYRE.—“Bougies Stéariques.” 2 vols. Paris, 1904.  
 G. HEFTER.—“Technologie der Fette und Oele.” Vol. III. Berlin, 1910. Gives an excellent and very complete account.

**Process of Candle Moulding.**—Candles consist of cylinders of wax or fatty acids surrounding a wick lying true in the centre in order to avoid unequal burning. These **wicks** are made of cotton threads loosely plaited together and soaked in a solution of boric acid, potassium nitrate or chloride, and ammonium chloride, sulphate, or phosphate. The plaiting causes the wick to curve when burning, and thus they burn away at the ends without causing the flame to smoke. The chemical solution vitrifies the ash of the wick, and the minute glassy particles dropping off from the bent wick leave the end free for the melted fat to ascend to the point where combustion is taking place. In the absence of this chemical treatment the wick burns off short in the flame and causes persistent guttering. Stearine or paraffin candles are moulded in special machines.

Fig. 27 represents an ordinary candle machine capable of moulding ninety-six candles simultaneously. It consists of a battery of moulds contained in an iron tank A, through which warm or cold water can be passed as desired in order to heat or cool the moulds.

Each mould (the construction of which is shown in Fig. 28) is made of polished tin, sometimes backed by iron, and traversed by a piston which can be raised or lowered so as to force the candle out of the mould. The wicks are wound upon the bobbins D (Fig. 27), and pass up the piston rods B accurately through the centres of the candle moulds as shown in Fig. 28, and end in the candles from the previous “round,” which are held in exact position in a special clamp. To use the machine hot water is first driven through the box containing the moulds so as to heat them to a suitable temperature; next the melted wax is poured into the trough, and not only completely fills the moulds, but leaves a sufficient surplus in the troughs to allow for contraction of material on cooling. Next the hot water is replaced by a stream of cold, which rapidly chills the moulds, and

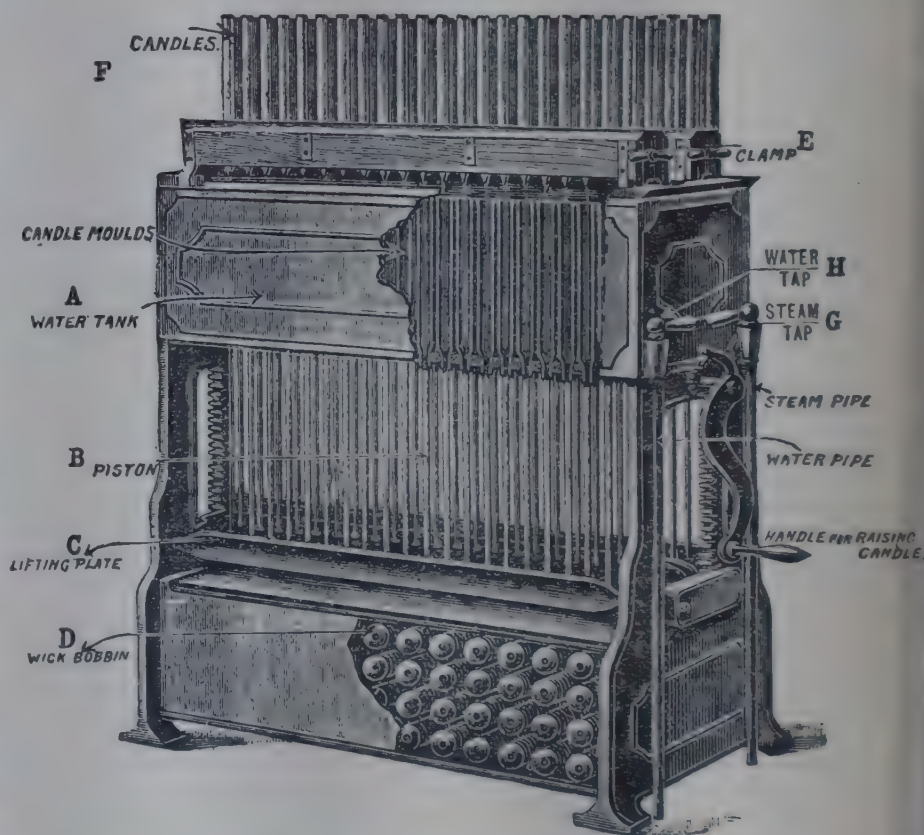


FIG. 27.—Modern Candle Moulding Machine.  
 (From J. Calderwood's "Manufacture of Candles," p. 15).



the candles solidify. The wicks of the candles held in the clamp above the trough are now cut, and the previous round of candles carried away for packing. The excess of candle material in the trough is now removed by means of a suitable tool, the emptied clamp replaced over the trough, and then, by operating the handle, the pistons B are pushed up the moulds, thus forcing out the candles into the holder

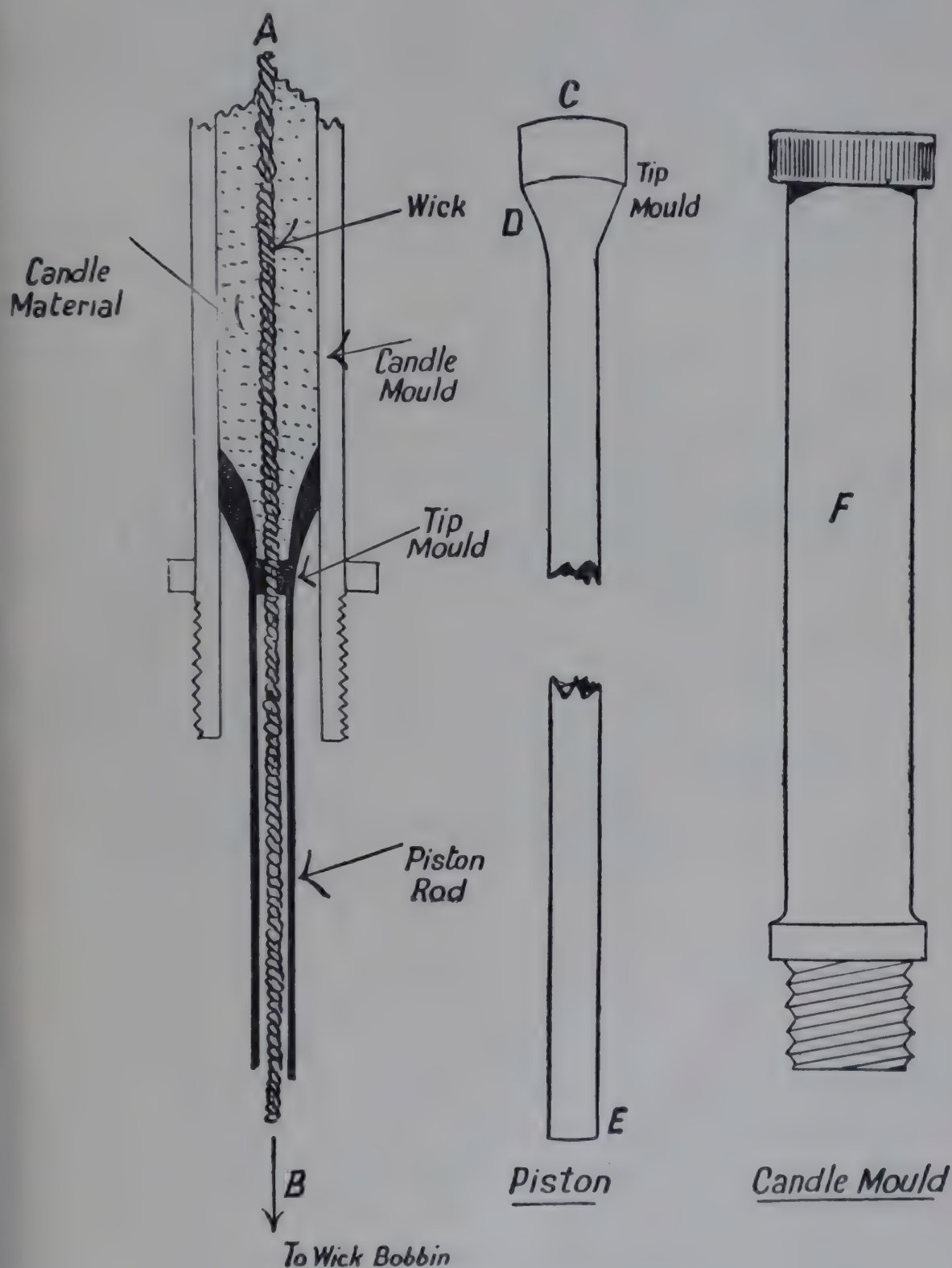


FIG. 28.—Section of Candle Moulds.

or clamp E. The wicks are drawn up with the candles, so that, immediately after the withdrawal of the first lot of candles, the pistons are lowered and another charge of wax poured into the moulds. When the surplus material in the trough is sufficiently solid, the wicks above are cut by a special knife or scissors, and the clamps containing the candles are then lifted away, and the candles ejected into a rack or

other convenient place. After the clamps have been replaced upon the machine the operation is continued until, ultimately, the bobbins D, which contain sufficient wick for several hundreds of candles, are emptied, when they are either rewound, or replaced by others.

A great advance on these machines is represented by Cowles' "Multiple" candle-moulding machines, which enormously increase the output and effect a very great economy of labour, water, steam, and floor space; thus while by the use of a small candle machine such as that just described ninety-six candles can be produced at one operation, by the use of a multiple machine of the same size no less than 360 candles can be produced by one operation. The "Multiple" machine is capable of producing no less than 518 candles at one filling, filling three times an hour, and producing per week of fifty-five working hours no less than 90,000 candles. It is fitted with patent swing-over clamps for holding the ejected candles, depositing them in a V-shaped tray attached to the clamps.

"Self-fitting" candles have conical fluted ends by which they may be fitted into any candlestick without scraping or paper. Being tapered at both ends they cannot be produced in a single mould.

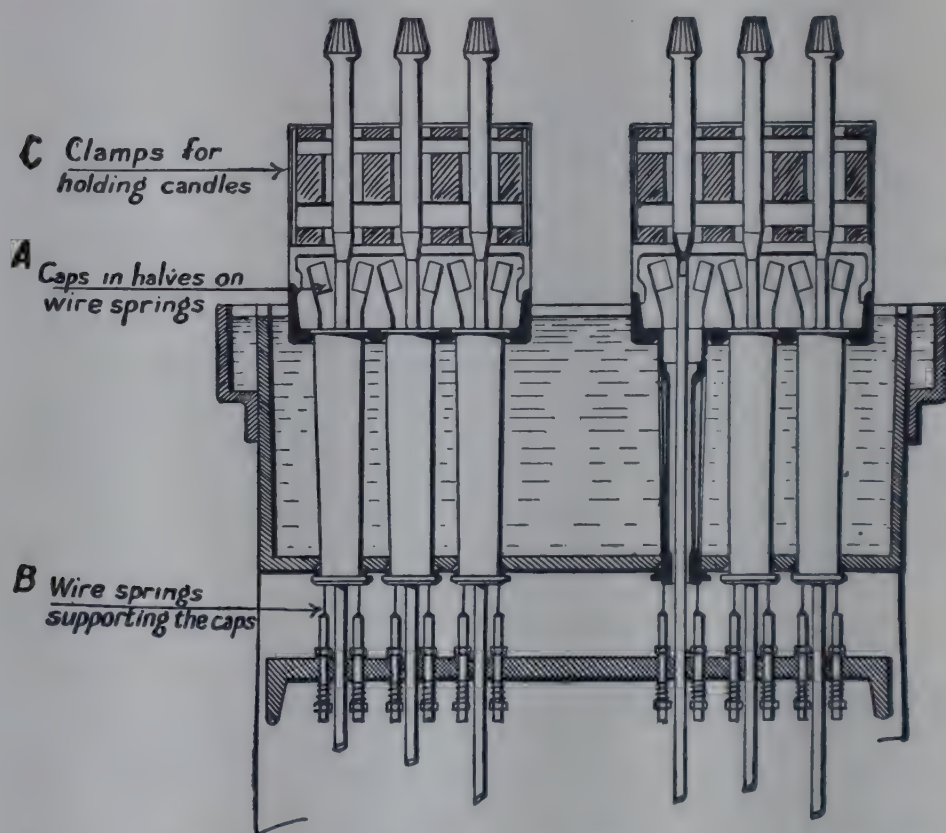


FIG. 29.—Durpitt's Machine for Moulding Candles with Self-fitting Ends.  
(By the Courtesy of Price's Patent Candle Co.)

Messrs Price's say that this machine (Fig. 29) proved unsatisfactory and has not been used for many years.

The arrangement used by Price's Patent Candle Company, and patented by their Mr Durpitt, is shown in the figure. The cap A, which forms a fluted conical butt, is in halves, each supported on wire springs B, which pass down recesses in the mould. When the candle is forced out of the mould these halved caps also rise a little, and springing apart they allow the enlarged butts of the candles to pass through; these are received in clamps C, and held in position over the centres of the moulds until the next lot of candles has solidified round the wicks, as in the ordinary "plain end" machines.

In some forms the conical ends are made by means of a movable top bed, fitted with moulds for these butts.

Usually a little paraffin is added to the stearine in order to render the wax less brittle. Also to paraffin candles varying amounts of stearine are added for similar reasons. Since low melting candle material is much cheaper than high melting material, candles are now manufactured with a thin exterior of any suitable high melting material, the interior being composed of the cheaper low melting material. Special machinery is required to perform the moulding, but the candles thus produced have the advantage of being very economical to manufacture, and not liable to gutter in burning, or cake together in packing, while the exteriors can be lettered for advertising purposes, or made of any desired colours, such colours not interfering with the combustion of the candle. **Wax** and **ceresin** candles are not moulded, because the wax at the moment of moulding shrinks away from the mould; also they stick to the form. Thick **altar candles** are made simply by



pouring molten wax down a wick hanging vertically, and then rolling between boards. Smaller candles of the same material are made by drawing the wicks repeatedly through melted wax until of the proper size. By mixing beeswax with varying proportions of paraffin and stearic acid it is possible to mould it like ordinary candles.

**Colouring Candles.**—The candle material is usually coloured, before moulding, with organic colouring matter, the best sorts being those soluble in alcohol, since they affect least the burning power of the candle. The stearine is melted at 65° C., and the dye stirred in. The quantity varies between 0.05 and 0.01 per cent. of the weight of candle material. Mineral colouring matters cause the candles to burn badly, while many aniline dyes fade rapidly when in contact with the stearic acid. Good results are obtained with the following dyes: *Red*—sudam IV., flexin, rose bengal, rhodamin. *Yellow*—chinolin yellow, auramin. *Green*—acid green, Victoria green. *Blue*—indulin, Victoria blue, methyl violet.

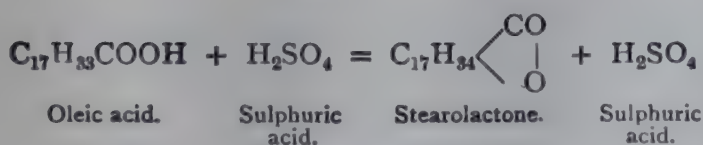
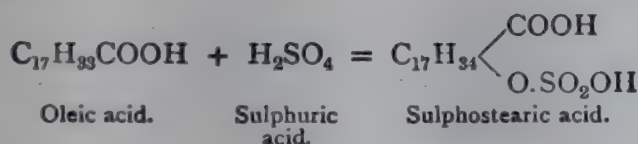
**Transparent Candles** for ornamental purposes may be made in a variety of ways. (1) If 100 parts of paraffin wax be melted at 80°-90° C. with 2 parts of beta-naphthol, a material is obtained which remains transparent on moulding. (2) Paraffin wax, 70, stearine, 15, and petroleum, 15, melted together, give a low melting-point transparent candle material. (3) Paraffin wax, 90, stearine, 5, and petroleum, 5, give a higher melting-point material somewhat less transparent than (2).

**Statistics.**—The value of candles imported into the United Kingdom in 1910 was 5,600 cwt. (value, £14,500; exported were 292,000 cwt. (value £485,200).

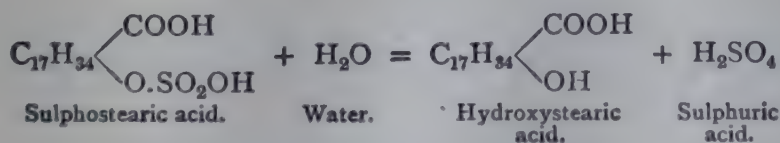
The United States in the same year imported 160,000 lbs., value \$26,000, and exported 3,215,000 lbs., value \$244,000.

**Manufacture of Candle Material from Waste Oleic Acid.**—Oleic acid, expressed from the stearic and palmitic acid used in candle-making, is a viscid fluid quite useless as a candle material. Many attempts have been made to turn it into candle material, but only the first process described has met with any measure of commercial success.\*

1. **The Conversion of Oleic Acid into Hydroxystearic Acid.**—Oleic acid is dissolved in distilled petroleum (60° Bé.), and cold concentrated sulphuric acid† run in, the temperature not being allowed to increase beyond 40° C. The following reaction takes place:



Next, live steam is blown in, whereby the sulphostearic acid is decomposed, thus:—



The steam-heated mass is allowed to stand, and the water and sulphuric acid, sinking to the bottom, are drawn off. The remaining mass is extracted with hot petroleum naphtha,‡ which dissolves out the hydroxystearic acid. On cooling.

\* See "The Conversion of Oleic Acid into Candle Material," by Dr Lewkowitsch, *Journ. Soc. Chem. Ind.*, 1908, p. 489. See also p. 100a.

† Zinc chloride has been also used for the purpose.

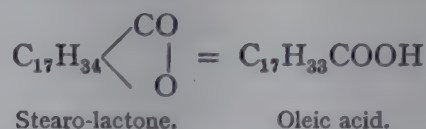
‡ U.S. Letters Patent, No. 772,129—N. M. Burton, patentee; Standard Oil Company, assignee—11th October 1904.



the petroleum the hydroxystearic acid separates out as a white mass, which is filtered, dried, and pressed.

Fifty per cent. of oleic acid is thus converted into hydroxystearic acid, two modifications of which exist—the alpha variety, melting at 77°-85° C., and the beta variety, melting at 81°-85° C.

The filtrate consists of stearo-lactone and unchanged oleic acid; when it is distilled the unchanged oleic acid passes over, and part of the stearo-lactone is converted into oleic acid or iso-oleic acid, thus:—



The recovered oleic acid is again treated with sulphuric acid as above described, and a further quantity converted into hydroxystearic acid. It is claimed that by this process no less than 85-90 parts by weight of hydroxystearic acid are obtainable from 100 parts of oleic acid.

Hydroxystearic acid used alone is not a good candle-making material, although its melting-point is high; but a mixture of 3 parts of the substance with 1 part of commercial stearic acid is used for stiffening paraffin wax candles.

For recent methods of converting oleic acid into hydroxystearic acid by treating with sulphuric acid, the reader may consult the following English patents:—

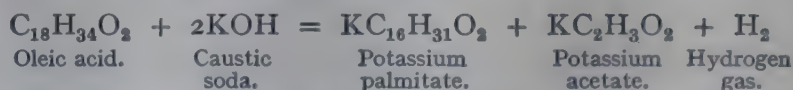
2,989, 1910.—**Dubovitz** treats benzine bone fat (1,465 kilos) with water (600 kilos) and MgO (8 kilos) in autoclave for eight hours; blows out, separates fatty acids and Mg soap from the glycerol water; dries fatty acids and Mg soap (1,412 kilos) and treats with 26 kilos of 92 per cent.  $\text{H}_2\text{SO}_4$  for one hour; boils with  $\text{H}_2\text{O}$ . The iodine number was lowered from 44.9 to 33.2, giving 12.9 per cent. of solidified oleic acid.

10,466, 1904; 10,466A, 1904; and 19,988, 1905.—**Dreymann** treats the oleic acid with  $\text{H}_2\text{SO}_4$ , then esterifies the separated acids with methyl alcohol, and separates the pure acids by distilling *in vacuo* their methyl esters (which boil at a lower temperature than the fatty acids themselves), and decomposing them again into methyl alcohol and fatty acid by superheated steam.

24,836 and 24,837, 1908.—**Barbé, Garelli, and Paoli** treat the oleic acid with concentrated  $\text{H}_2\text{SO}_4$ , and convert the resulting anhydrides and lactones into acids by saponifying with ammonia (English Patents, 12,210, 1907; 9,758, 1908), decomposing the resulting ammonia soaps with cold water. The ammonium oleates are more soluble in cold water than the ammonium stearates, and consequently are drawn off in solution from underneath the stearic acid and stearic soaps, and a separation is thus effected of the oleic and stearic acids, the ammonia soaps being finally decomposed by boiling water, the ammonia recovered and used again, and the free fatty acid drawn off. They claim to obtain from oleic acid about 65 per cent. stearic acid melting at 70° C. (see also pp. 93, 109).

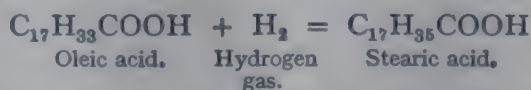
393, 1902.—**Sandberg** treats train oil with  $\text{H}_2\text{SO}_4$  and nitrous acid. The nitrous acid converts the liquid oleic into solid elaïdic acid,  $\text{C}_{18}\text{H}_{34}\text{O}_2$ .

2. **Conversion of Oleic Acid into Palmitic Acid.**—When oleic acid is fused with caustic alkali it is converted into palmitic acid, thus:—



On acidifying the aqueous solution with dilute sulphuric acid, the palmitic acid is precipitated as a white crystalline mass. Candles made of palmitic acid manufactured by this method have actually appeared on the market, but the process was not commercially successful, the evolution of hydrogen making the manufacture dangerous, while the candles themselves possessed an unpleasant smell and greasy touch.

3. **Conversion of Oleic Acid into Stearic Acid.**—Oleic acid is an unsaturated acid, only differing from stearic acid by the absence of two hydrogen atoms. Several processes have been proposed for making oleic acid take up these two hydrogen atoms and become stearic acid according to the equation:—



The processes are described in the next article on the **Hydrogenation of Fats**.

**Acknowledgments.**—The author's best thanks are due to Messrs Price's Patent Candle Company for much information regarding a subject which they, more than any other firm, have improved and developed. Also to Mr W. H. Stephens for much information regarding recent processes.



# THE HARDENING OF FATS

## HYDROGENATION OF FATS

BY GEOFFREY MARTIN, Ph.D., D.Sc., F.R.I.C.

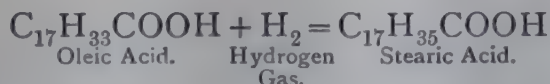
### LITERATURE

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- HENDERSON.—"Catalysis in Industrial Chemistry," London, 1919.
- MAXTED.—"Catalytic Hydrogenation and Reduction," London, 1919.

The following important patents should also be consulted:—

- English Patents**, 1,515, 1903; 2,520 and 13,042, 1907; 9,112, 1908; 7,726, 3,752, 29,612, and 30,282, 1910; 5,188, 13,519, 15,439, 25,326, and 15,440, 1911; 72, 4,702, 5,773, 18,282, 18,310, 18,996, 18,998, 22,092, 23,377, 23,643, 24,084, 27,718, 28,754, 28,981, 1912; 4,144, 10,204, 11,542, 11,543, 13,382, 16,283, 16,782, 18,350, 1913; 2,306, 2,307, 3,344, 3,865, 4,665, 5,967, 15,668, 16,600, 1914; 109,993, 1917.
- German Patents**.—211,669, 1907; 221,890, 1910; 236,488, 1911; 260,885, and 256,500, 1913.
- French Patents**.—450,703, 1912; 458,445, 1913.
- U.S.A. Patents**.—902,177, 1908; 1,004,034, 1911; 1,004,035, 1911; 1,040,531, 1,040,532, and 1,043,580, 1912; 1,059,720, 1,058,738, 1,060,673, 1913.

Oleic acid is an unsaturated acid only differing from stearic acid by the absence of two hydrogen atoms. Several processes have been proposed for making Oleic Acid take up these two hydrogen atoms and become stearic acid, according to the equation:—



Thus fuming hydriodic acid reduces oleic acid to stearic acid; so does heating with iodine; other attempts to reduce oleic acid to stearic acid have also been successful. For details of these and other new processes the reader is referred to the *Journal of Chemical Industry*, 1908, vol. 27, p. 489.

Recently it has been shown that when Oleic Acid is treated with nickel powder in the presence of hydrogen, it takes up hydrogen and gives an almost theoretical yield of hard stearic acid.

Moreover, this latter action is of general importance. Not only does oleic acid, but also liquid *unsaturated fats* take up hydrogen under these conditions and become converted into hard substances. Thus the liquid glyceride, triolein, is converted into solid tristearin:—



Sabatier and Maible (*Ann. Chim. Phys.*, 1909, [8], 16, 73) showed that oleic and elaidic acids, when treated with hydrogen in the presence of *reduced* nickel at 280°-300° C., yielded stearic acid. The nickel, technically prepared by reducing nickel carbonate *in situ*, is thrown into the boiling fat and H gas is passed through.

The first patents referred to the passage of hydrogen gas through *the vapours of fatty substances*. Such processes were of little use in the case of glycerides, as they are decomposed when vapourised.

The fundamental patent was taken out by Norman (English Patent, 1,515, 1903), which described the hydrogenation of oils in a liquid condition, by merely passing a current of hydrogen into the oil, heated to a suitable temperature, and containing a finely divided metal as catalyst.

This patent is fundamental in character since it precluded all other manufacturers from hydrogenating oils in the liquid condition. In 1913, however, it was declared to be invalid owing to the meagre information given in the patent.

Recent work has been principally directed towards the preparation of the catalytic nickel in a suitable state, the best proportion of catalyst to use, the best temperature of hydrogenation, the proper refining of the fatty body, the application of continuous mechanical agitation, the purification of the hydrogen.

For details of these the reader must consult the patent literature above referred to. Published details are meagre. Crossley (*loc. cit.*) gives details for rape oil, whale oil, etc., which were published in the lawsuit of Joseph Crosfield & Sons Ltd. v. Technico-Chemical Laboratories Ltd.

The method was invented by Sabatier and Senderen. The reader will find a résumé of their researches in the *Annales de Chimie et de Physique*, 1905, [8], 4, 319; 1909, [8], 16, 70. See also *Sabatier, Ber.*, 1911, 44, 1984; Sabatier, "La Catalyse."

An excellent account is also given by Crossley, *The Pharmaceutical Journal and Pharmacist*, 1914, 92, pp. 604, 637, 676. See also C. Ellis, *J.S.C.I.*, 1912, 31, 1155; also his book, "Hydrogenation of Oils," 1914; T. Shaw, *Ibid.*, 1914, 33, 771.

**Theoretical.**—At constant temperature and pressure the velocity of hydrogenation of an oil is given by the equation:—

$$V = K.C_1C_2.$$

Where  $V$  is the velocity of the reaction,  $K$  the constant of reaction,  $C_1$  is the active mass of the oil, and  $C_2$  the active mass of the hydrogen.

Consequently, in designing a plant for the hydrogenation of oil it is essential that the product  $C_1C_2$  should be as large as possible. In other words, the product of the number of pounds weight of hydrogen per minute driven against the oil into number of pounds of oil it meets per minute must be as large as possible.

Hence the hydrogen should be highly compressed, as in this way a larger weight is concentrated in a given volume. Also the speed with which the oil and hydrogen circulate in the system in a counter-current direction should be as great as possible. Hence the pumps should be powerful, and it is theoretically a mistake to depend upon gravitation and ordinary pressures for the flow of gas and oil. The great practical advantage of the latter arrangement is ease of working.

It is also well known that an increase of pressure favours the formation of products possessing a smaller volume than the original components. Since the hydrogenated oils occupy less volume than the original hydrogen and oil mixture, on this ground also (see below) it is advisable to use high pressures and powerful pumps.

The reaction is *mono-molecular*. Fokin (*J. Russ. Phys. Chem. Soc.*, 1908, 40, 276) has shown that the saturation with hydrogen of a double bond at constant temperature and pressure follows the ordinary mono-molecular formula:—

$$K = \frac{1}{t} \log_e \frac{a}{a-x}.$$

Where  $a$  represents the total volume of hydrogen absorbable by the unsaturated oil, and  $x$  the volume of hydrogen actually absorbed after the time  $t$ .

The reaction starts rapidly, but slows down as saturation is attained, following in this the ordinary mono-molecular formula:—

$$\frac{dx}{dt} = K(a-x).$$

The saturation of an oil with hydrogen is *exothermic*, i.e., attended with the evolution of heat. Maxted ("Catalytic Hydrogenation and Reduction," pp. 95 and



97) states that, in the course of a two hours' run, a charge of oil will have spontaneously increased its temperature from 140° to 185° C.

If  $Q$  be the heat of reaction and  $K$  the equilibrium constant,  $K$  is dependent upon the temperature according to van't Hoff's equation:—

$$\frac{d \log K}{dT} = \frac{Q}{RT^2}$$

Consequently  $K$  tends to diminish with rise of temperature, and for this reason it is advisable to carry out the hydrogenation at as low as possible a temperature compatible with a sufficient practical velocity of reaction. The formation of bodies whose production is attended with the evolution of heat (*i.e.*, exothermic bodies) is checked by rise of temperature.

### Practical Conditions of Success.

It has been found that the main conditions for success in the hydrogenation of oils in the liquid condition are:—

1. **Exact Control of the Temperature**, *e.g.*, the reduction of the oil with nickel must take place at as low a temperature as possible—say 140° C. to 180° C.—in order to avoid decomposing the oil and giving it a bad taste and colour. Again the nickel must be reduced at a low temperature (see below).

2. **The Purity of the Reacting Bodies**, *e.g.*, the *fats* should be purified by removing free fatty acids (not more than 1 per cent. free fatty acid should be present) and moisture, sulphur compounds, etc.

The *nickel* must be pure (see below). The *hydrogen* must be extremely pure if good results are to be attained. The purer the hydrogen the more rapid the reduction. Sulphur compounds, arsenic, water, carbon monoxide, in the hydrogen all diminish its activity in the presence of nickel.

3. **The Exclusion of "Catalytic Poisons,"** *i.e.*, substances which destroy the hydrogenating action of the nickel catalyst.

Chlorine, sulphur (as sulphide), phosphorous, and arsenic are the worst of these catalytic poisons. Oxygen and water and carbon monoxide also affect injuriously the activity of the nickel.

4. **The Fine State of Division of the Catalyst.**—The more finely divided the catalyst the more rapid the action.

5. **The Pressure of the Hydrogen Gas.**—Several processes exist in which the hydrogenation takes place under ordinary atmospheric pressure, and it is true that if the catalyst is sufficiently active an almost instantaneous conversion of the oil is possible. Nevertheless, in general the higher the pressure employed the more rapid and effective the hydrogenation; four atmospheres is a good working pressure. Bergius (*Zeit. Angew. Chem.*, 1914, 27, 522) actually showed that the hydrogenation of oil can be affected without catalytic aid by the use of high temperatures and very high pressures.

In general a catalyst only acts in accelerating a chemical action which takes place of itself at a sufficiently high temperature and pressure.

It is a well-known law of physical chemistry that an increase of pressure favours the production of reaction products, having a smaller volume than the products we start with. As the hydrogenation of fats is attended with the absorption of hydrogen so that the resulting hydrogenated oil occupies a smaller volume than the hydrogen and oil we start with, this result of Bergius is to be expected on theoretical grounds.

6. **An Adequate Intermingling and Mixing of the Hydrogen and the Oil.**—It is obviously essential to mix the hydrogen and oil effectively by means of stirring gear or other devices.

This need of mixing has probably been exaggerated in the patent literature. The hydrogen can only act by solution in the oil, and the nickel, once wetted by the oil, cannot come into contact with the gas except by solution; so that all that is needed is a gentle mixing of the contents. Very rapid diffusion also aids the action. Hence the large number of patents which describe complicated devices for bringing hydrogen and oil into intimate contact by violent agitation, or "atomisation," are probably introducing needless elaboration into the plant necessary for successful treatment of oil with hydrogen.



It has been shown that the activity of the nickel catalyst depends upon:—

**1. The Purity of the Nickel.**—For example, in preparing the nickel from nickel sulphate by precipitating as nickel carbonate by means of sodium carbonate, and then reducing the latter in hydrogen, it is absolutely essential to wash the nickel carbonate after precipitation until it is quite free from all traces of sulphate. Sulphur compounds affect the activity of the catalyst very badly, and consequently some authorities prefer to work with nickel nitrate, precipitating it as nickel hydroxide by caustic soda, washing, drying, and reducing.

**2. The Temperature of Reduction.**—It is necessary for the nickel to be extremely finely divided so as to be in a pyrophoric condition, *i.e.*, the metal spontaneously inflames on contact with air or oxygen. This condition is only attained by carrying out the reduction with hydrogen at as low a temperature as possible. Thus nickel oxide begins to reduce at 200° C. Reduction is incomplete below 270° C. The usual temperature employed is 300° to 320° C. Too high a temperature of reduction (say 400° C.) converts the nickel into an almost inactive modification. Nickel carbonate is said to be sufficiently reduced at 230° C. (see Fuch's patent, English Patent 11,542, 1913), *i.e.*, a lower temperature than is necessary with the oxide.

Organic salts of nickel can be reduced at still lower temperatures (see Wimmer-Wiggins Patents; see English Patents, 25,326, 1911; 4,144, 1913).

**3. Protection from Oxidation.**—The finely divided nickel after reduction must not be allowed to come into contact with air, otherwise it oxidises and becomes inactive. It is therefore either kept in an atmosphere of hydrogen until use, or else dropped into oil immediately after reduction, and kept in that way. In some processes the nickel carbonate is reduced in the oil itself. (See below.)

**4. Use of Nickel Carbonyl.**—Shukoff (German Patent, 241,823, of 18th January 1910) employs an entirely different method of preparing the nickel catalyst. He passes *nickel carbonyl* (obtained by action of carbon monoxide on reduced nickel at a low temperature) into oil heated to 200° C.

The nickel carbonyl is decomposed and metallic nickel is set free. Lessing's process (see English Patent, 18,998, of 1912) uses this fact for his process of hydrogenation.

**5. Use of Carriers for Nickel.**—In order to increase the catalytic effect of a given quantity of nickel a large number of patents have been taken out for the use of carriers. Thus, pumice, kieselguhr, asbestos, and other porous bodies are impregnated with nickel salt, and the whole reduced with hydrogen.

Modern practice, however, has tended to diminish the use of these carriers. They aid filtering off the nickel.

Many proposals have been put forward for increasing the *activity* of the hydrogen used in reducing the fat.

Thus Fuch (English Patent, 11,543, 1913) suggests:—

**1.** Heating the hydrogen to 200°–250° C.—a higher temperature than that of the fat to be reduced.

**2.** Dissociating the hydrogen into atoms by treating it with chemically active rays.

**3.** Passing the heated hydrogen over a catalyst such as spongy platinum or freshly prepared nickel, which appears also to increase the chemical activity of the hydrogen.

For use of electrical discharges, chemically active rays, etc., in increasing the activity of the reacting materials (see Utescher, British Patent, 20,061, 1912), where the use of mercury vapour lamps is suggested. In this connection see also *Seifen Ztg.*, 1913, p. 851; F. Gruner, French Patent, 453,664, 1913. In the latter patent oils and fats are subjected to the action of an electric current of very high tension and frequency. 50,000 to 100,000 volts are mentioned. Farmer and Parker (*Journ. Amer. Chem. Soc.* (1913), p. 1524) describe experiments on the effect of ultraviolet light on colloidal platinum.

**Use of other Metals than Nickel.**—In addition to nickel and its compounds, colloidal platinum (Fokin, Willstätter), and palladium (Paul), copper and iron may be used. Palladium has been used industrially in amounts as small as  $\frac{1}{100000}$  to  $\frac{1}{1000000}$  of the amount of fat (see Paul and Skita, German Patent, 230,724; *Ver. Chem. Werke, A.G.*, German Patent, 236,488, 1919; British Patent, 18,642, 1911; palladium chloride (with rubber or gelatine as protecting colloid) is used. Reduction with platinum or palladium takes place at a lower temperature than when nickel is used.

**Supply of Hydrogen for Hydrogenating Fats.**—One ton of oleic acid requires about 79,000 litres (2,800 cubic feet) of hydrogen. One ton of Triolein (*e.g.*, the glycerine of oleic acid) requires 75,900 litres (2,680 cubic feet) of hydrogen.

The production of hydrogen for this purpose is fully described in Martin's "Industrial Chemistry, Inorganic," vol. I., to which the reader is referred for fuller details.



It might be mentioned here that the hydrogen is mainly prepared by the following methods:—

1. **Electrolytic.**—This method produces a very pure gas, but is too expensive to compete with the other processes except in countries like Norway, where water power is cheap, and where this process actually is the dominant method of producing hydrogen.

2. **Iron Sponge Steam Process.**—Oxide of iron is reduced by means of water gas carefully purified from sulphur compounds. Steam is then passed over the heated reduced metal, yielding iron oxide and hydrogen. The oxide is again reduced by water gas.

**Lane's Plant** (Lane of Ashford, Middlesex, England) is one of the best-known and successful plants for working this process. **Maxted** (Gas Developments, Ltd., Walsall, Birmingham) have modified this process so as to produce a gas as pure as electrolytic hydrogen but at less cost.

3. **The Harger-Terry Process** (see British Patent, 6,007, 1917) consists of impregnating impure hydrogen with the proper amount of electrolytic hydrogen and oxygen, and passing the resulting mixture over a suitable heated catalyst. The carbon monoxide, sulphur, and phosphorus compounds are oxidised, and absorbed by lime or alkali. The resulting hydrogen is exceedingly pure.

**The Linde-Caro Process.**—Water gas is liquified and the hydrogen separated from the CO by fractional distillation. The gas used for hydrogenation consists of H=95-97 per cent., CO=2 per cent., rest=N. The pumping is done by a gas engine utilising the separated CO as fuel.

The hydrogen used must be free from H<sub>2</sub>S, 0.1 per cent. being sufficient to destroy the catalytic activity of nickel.

In 1913 the Linde Co.'s plants for producing H for the hardening of fats (*Zeit. Angew. Chem.*, 1913, 26, III. 814; see also Vol. II., "Industrial Hydrogen" yielded enough H to harden 100,000 tons of fat.

**Whale Oil** is the chief oil subjected to hydrogenation, the world's supply in 1912 amounting to 1,200,000 barrels (42,000 tons). (See *Offerdahl, Ber. deutsch. Pharm. Ges.*, 1913, 23, 558, who states that there is a factory in Norway capable of producing 4,500 tons of H by an electrolytic method, and of hardening 150 tons of whale oil per twenty-four hours.)

Hardened whale oil melts at 40°-50° C., is devoid of taste and smell, and so is a valuable fat. Linseed oil is also largely hardened.

**Industrial Processes for Hardening Fat.**—A very large number of processes have been described in the patent literature, but very few have proved technical successes. The reason is that considerable technical difficulties occur, especially in working on the large scale, and many of the patents describe processes in which these difficulties have proved insuperable.

**Description of Processes.**—Hydrogenation processes involving the use of nickel may be divided into three classes:—

- (1) Dry processes.
- (2) Wet processes.
- (3) Gaseous processes.

1. **Dry Processes.**—In these the catalyst is produced by treating the oxide of nickel in a dry state with hydrogen gas at a temperature of about 300° C.

The reduction of the nickel is attended with many difficulties. In the first place, in the furnace a stirring apparatus is required in order to mix the nickel oxide thoroughly with the hydrogen. Hence the employment of rotary drums, stirring autoclaves, etc., the heating of which presents several difficulties. Again the sensitiveness of the catalyst depends very largely upon the temperature.

If the temperature is too high (400° C.), the nickel will pass from the catalytically active black form into the inactive gray modification. The lower the temperature of reduction the more active the nickel. But if the temperature of reduction is too low (*i.e.*, below 250° C.) the reduction of the nickel is imperfect.

Consequently the temperature of reduction has to be very carefully regulated, and this is a difficult matter to effectively control.

The reduced nickel, also, is very chemically active, and if not protected from oxidation, will lose its catalytic power. Also the opening of the reducing apparatus may be dangerous, as the reduced nickel will take fire in air, and if hydrogen is present in sufficient quantity this may cause an explosion—as has actually occurred in practice. Hence before opening the apparatus the hydrogen must be swept out by an inert gas like carbon dioxide.

The catalyst, when made, must also be employed under exactly defined conditions.

Some workers consider that nickel reduced in the dry state is too compact to be used as such, and so they place it on special "supports," such as clay, asbestos, etc. These materials obviously add to the difficulty of regenerating the nickel, and it has been stated that they may give to the fat an earthy taste and bad colour. Moreover, much fat is absorbed in their pores, the recovery of which is difficult.



Finally, the catalyst is mixed with the mass of oil to be hardened, and while actively agitated hydrogen gas, under a pressure of 4 to 5 atmospheres, is heated to a suitable temperature, say  $140^{\circ}$  to  $250^{\circ}$  C.

The following works have been stated to be using processes of this type:—

<i>Process.</i>	<i>Works.</i>
NORMANN - . . . .	Germaniawerke, Emmerich. Schichtwerke, Aussig. Jurgene, Ose.
WILBUSCHEWITSCH . . . .	Lever Bros., Port Sunlight. Bremen-Bersigheimer, Oelfabriken. De No Fa, Fredriksstad. United Soap Works, Zwinndrecht. "Salolin," Petrograd and Nischni-Novgorod.
CARLTON ELLIS . . . .	Hydrogenated Oil Co., New York. Southern Cotton Oil Co., New Jersey and Georgia.
C. E. KAYSER . . . .	Procter Gamble Co., Cincinnati.

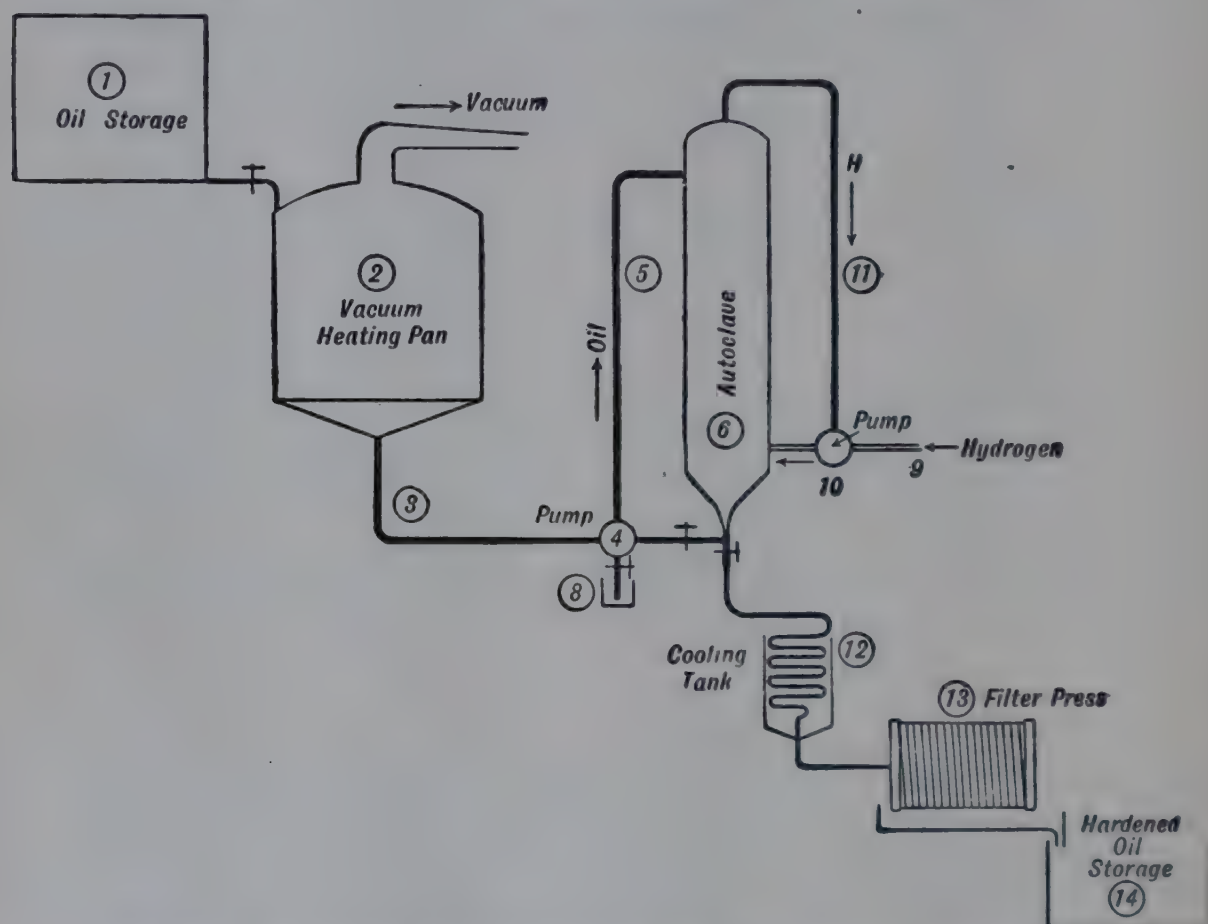


FIG. 294.—Dry Process for Hydrogenating Fats. (Normann.) (See p. 100f.)

The following details give a rough outline of the methods employed in this process. Plant and autoclaves are sold by Lane (Ashford, Middlesex, England), and also by Maxted (Gas Developments Ltd., Walsall, near Birmingham, England) for these processes.

**Normann Processes.**—The following is a brief account. For fuller details and descriptions of autoclaves, etc., see Geoffrey Martin, "Oil, Fats and Waxes."

The fat to be hardened must contain less than 1 per cent. of free acids, otherwise nickel soaps will be formed, and nickel will appear in the refined fat. Hence before hardening the fat should be refined, as this will pay in the end. The fat must be dry. For this purpose it is run from a storage tank 1 into a vacuum heating pan 2, and is there heated until water is eliminated. It is then run down the pipe 3 and forced by the pump 4 up the pipe 5 into a heated autoclave 6. This autoclave is steam-heated, and is kept at a temperature of about  $140^{\circ}$  C. The pressure inside the autoclave is about 5 or 6 atmospheres. The interior is usually fitted with baffle plates and sometimes with stirring gear, so that the liquid in pouring down the interior of the autoclave is very intimately mixed with an ascending stream of hydrogen gas. The fat reaching the bottom of the apparatus is



pumped by 4 up the pipe 5 and in again at the top of the apparatus, so that a continual circulation of the fat is produced until the degree of hardening required is attained.

The hydrogen gas is drawn into the apparatus through the pipe 9, and by means of the pump 10 it is forced into the bottom of the apparatus, and passes up the autoclave against the descending stream of liquid fat, and is intimately mixed with it. The unabsorbed hydrogen collects at the top of the apparatus and then passes down the pipe 11, and once again is injected into the apparatus by the pump 10.

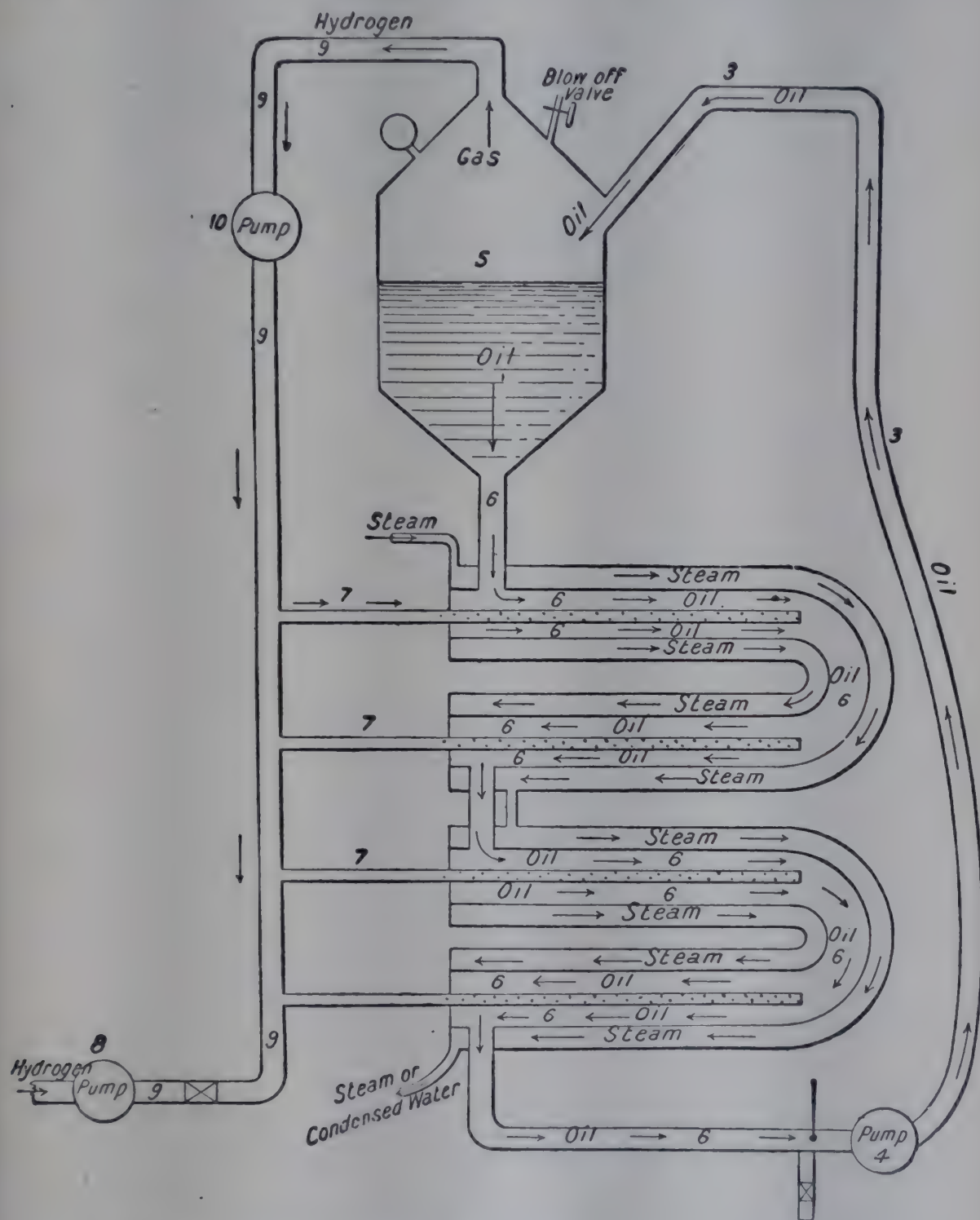


FIG. 29b.—Geoffrey Martin's Oil Hydrogenation Process. (See p. 100h.)

As the hydrogen is absorbed fresh supplies are passed in through the tube 9.

The catalyst is supplied as follows:—Nickel carbonate (made from nickel sulphate) is placed in a furnace and calcined. It is then ignited in a stream of hydrogen gas, so that it is reduced to the state of a metal in a finely divided condition. While still hot, and in an atmosphere of hydrogen, the charge of nickel is quenched in oil contained in a receiver. The oil containing the proper charge of nickel is then pumped from the vessel 8 into the autoclave 6 through the pump 4. It thus mixes with the charge of fat, and supplies the correct amount of nickel for the charge.

The hydrogenation proceeds rapidly, and is carried on until the iodine value sinks to about 60. It is important that the fat should not be too hard for edible purposes. The melting point of such fats should always be lower than that of the human body.

The nickel is usually recovered by running the fat out of the autoclave through partial coolers 12, so as to reduce its temperature somewhat (in order to avoid damaging the filter cloths), and it is then pumped through a filter press 13, into the storage tank 14, and the finely divided nickel is recovered and either sold as such to nickel manufacturers, or else it can be worked up again into sulphate.

The hydrogenation begins at about 140° C. with pure hydrogen, and the temperature then rises somewhat (the action being exothermic) up to 180° C. The lower the temperature is kept the better the resulting fat for edible purposes.

**Geoffrey Martin's Process.**—A new principle for mixing and heating the oils was introduced by Geoffrey Martin in an English Patent applied for on the 16th July 1918. In this apparatus all mixing gear, baffle plates, etc., are avoided in a very simple manner. The apparatus is shown in Fig. 29*b*, p. 100*g*.

The charge of oil (which may have been preheated to a suitable temperature) is placed in a reservoir 5, whence it flows down a series of tubes 6, 6, 6, which may be horizontally placed or vertically placed. These tubes are heated by a steam jacket (as is shown in the attached diagram). The oil flowing down the pipe 6 is

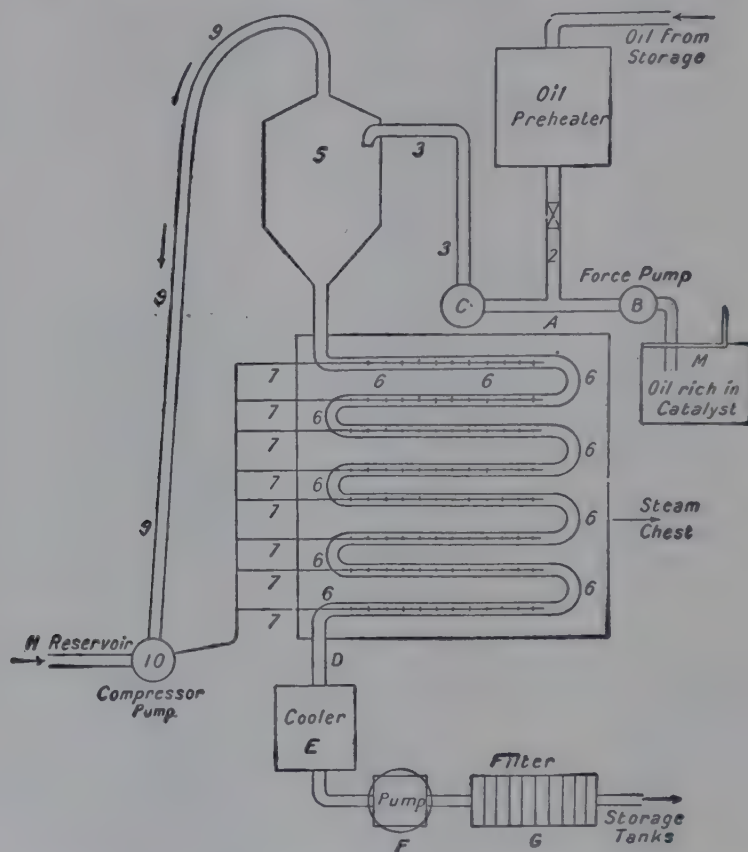


FIG. 29*c*.—Geoffrey Martin's Continuous Oil Hydrogenation Process. (See p. 100*i*.)

sucked in by the pump 4 and thrown up the pipe 3 back again into the reservoir 5, so that the oil is maintained in continual circulation through the reservoir and pipes.

The heating of the oil is thus effected not in the reservoir 5 but by means of the steam jackets surrounding the pipes 6. As the pipes can be made of any length the heating of the oil can be made to take place very rapidly, and the temperature of the heated oil is regulated by a thermometer or thermoinicator in the pipe as shown.

The mixing of the hydrogen with the oil is also effected in the pipes 6, 6, 6 as follows:—Projecting into the pipe 6, 6, 6 is a series of perforated pipes 7, 7, 7, closed, or partially closed, at each end. The hydrogen gas is forced by the pump 8 into these pipes through the pipe 9 until the requisite pressure of hydrogen is attained. The circulation of hydrogen in the apparatus is maintained by the pump 10 which draws the gas from the top of the vessel 5 and forces it down the tube 9 and then into the tube 7, where the gas rushes out through the perforations into the descending oil, so that there is a continual circulation of oil going on in the one direction and a



stream of hydrogen passing up through the oil in the other. As the pipes are narrow the hydrogen and oil are very intimately mixed in the pipes, thus rendering unnecessary the use of baffle plates, stirring gear, and similar plant for the purpose.

In a second patent applied for on 27th November 1918 (19,567, 1918), Geoffrey Martin makes his process continuous. The apparatus is shown in Fig. 29c, p. 100h. The oil to be hardened is pumped in a steady stream into a pre-heater 1, and then flows out in a carefully regulated stream through the tube 2. At the point A it meets the oil from the tank M, which oil is forced in through a force pump B. The oil in M is impregnated with catalyst, and consequently, the oil containing catalyst mixes with the larger volume of oil devoid of catalyst coming from the pre-heater 1, and the rate of flow of oil from M and from the pre-heater 1 is so regulated that proper amounts of catalyst are introduced into the oil so as to cause hydrogenation to take place properly. The oil now mixed with catalyst is pumped by means of C up the tube 3 into a reservoir 5, and continuously flows down a series of tubes 6, 6, 6, which may be of very considerable length, and which are heated externally by steam, hot air, or other heating

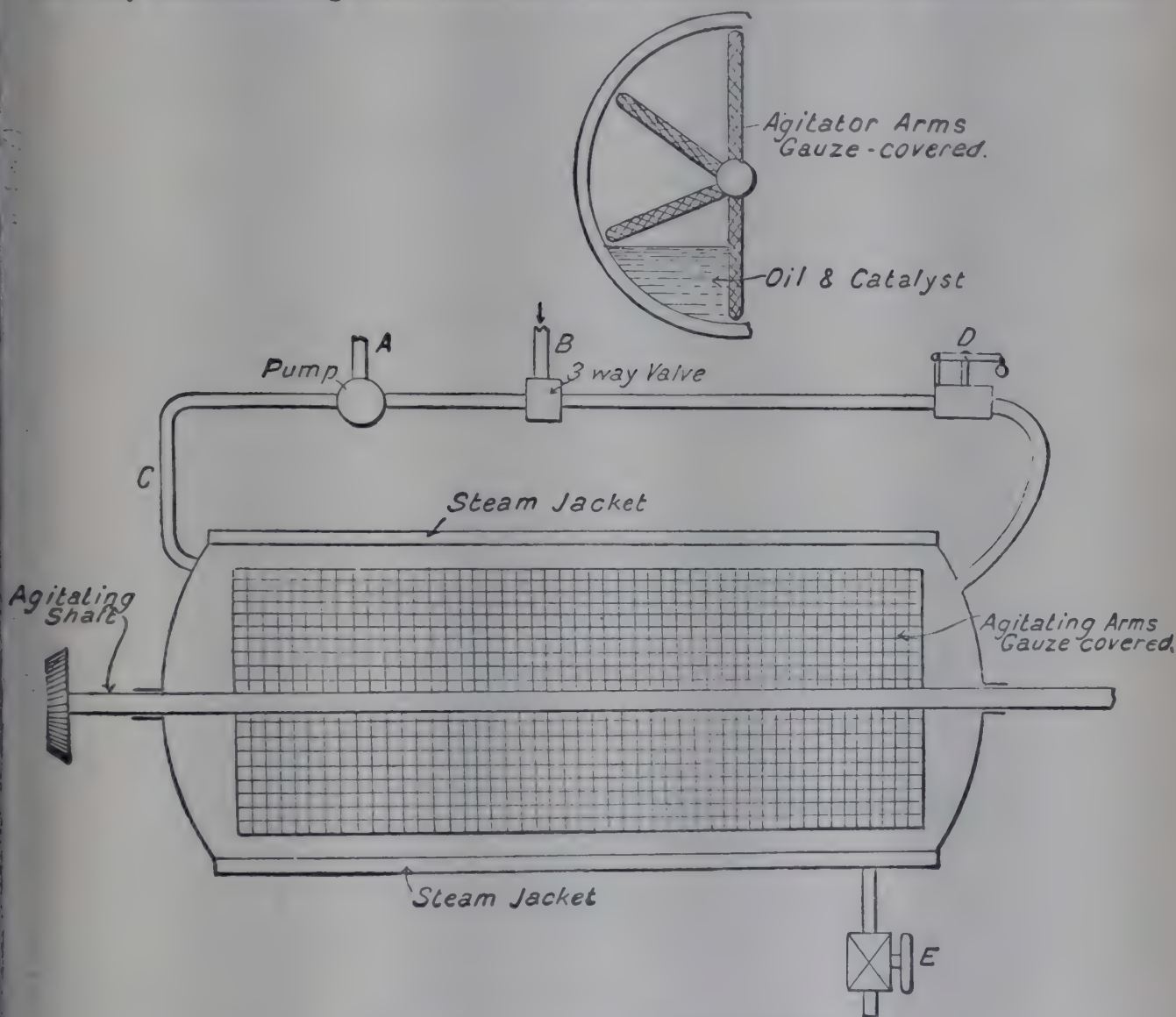


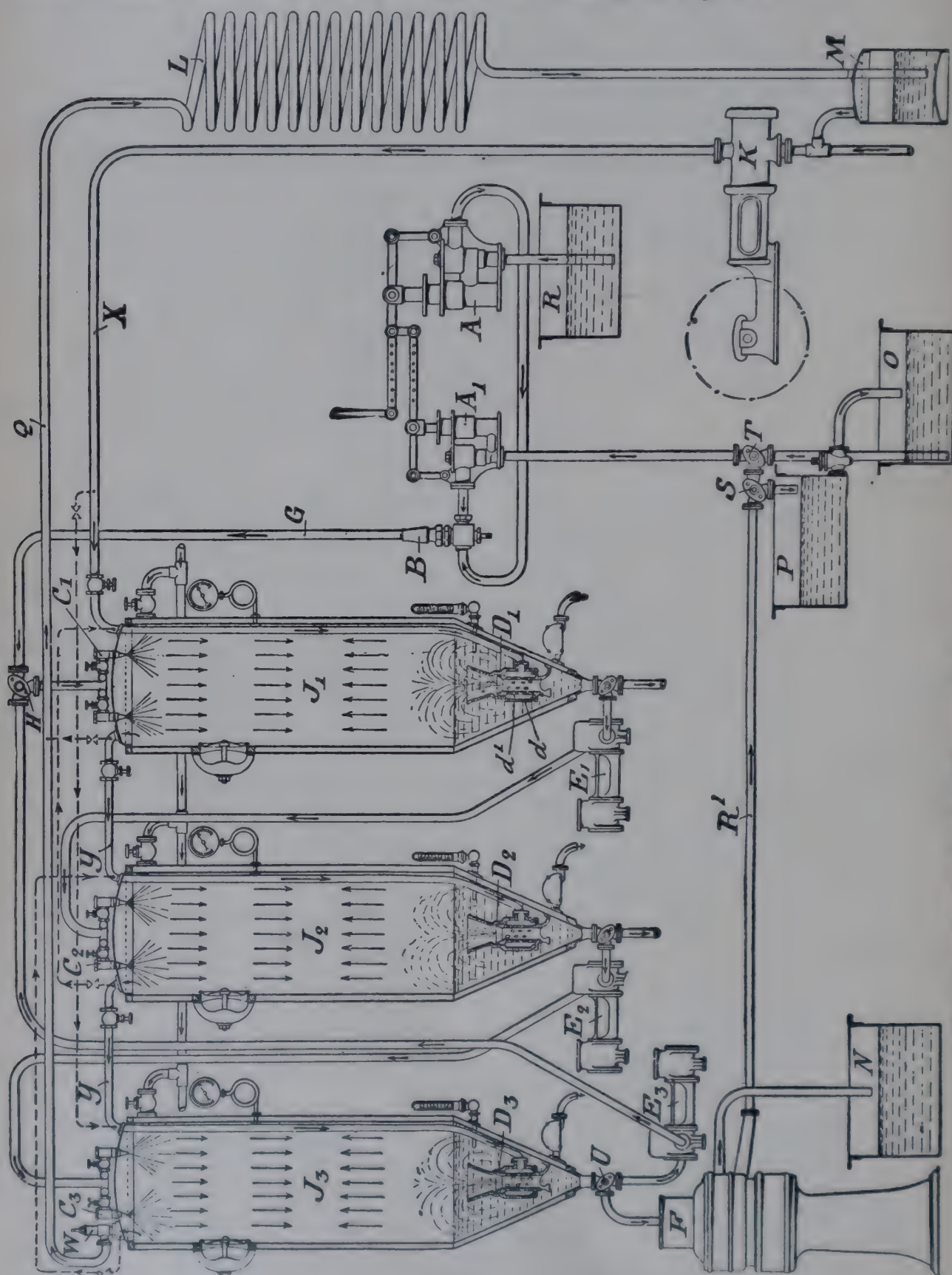
FIG. 29d.—Kayser Process for Hydrogenating Oil.

medium. Inserted into each of the tubes 6, 6, 6 is a series of perforated pipes 7, 7, 7, through which the hydrogen is forced, and which churns up and mixes with the oil as it flows down the tubes as described in the previous patent. The oil, by the time it has passed through all the tubes and has reached the outlet D, is hardened sufficiently, and passes away through the cooler E, and then is forced through a pump F to a filter-press G or other arrangement for removing the catalyst. From G it passes to the storage tanks. The rate at which the oil is hardened depends upon the length of the pipes 6, 6, 6, through which it passes, and the quantity of hydrogen gas it meets in passing down the pipes. Also the purity of the hydrogen and the sensitiveness of the catalyst are important factors. Consequently, by making the passage through the pipes 6, 6, 6 sufficiently long, and causing it to meet a sufficient quantity of hydrogen during its passage, the oil emerging at E can be hardened to any required degree.

The advantages of a continuous counter-current process are obvious. In ordinary processes large masses of oil, weighing a ton or more, are treated in batches in massive autoclaves, whereas in the present process the oil is fed in a thin stream through long tubes, without at any moment

of time, a great mass of oil being under treatment. Thus danger of explosion or fire are largely obviated.

The Kayser Process (United States Patent, 1,004,035, 1911) consists in mechanically agitating the oil and catalyst in presence of hydrogen under pressure. The apparatus described in the patent is shown in Fig. 29d, p. 100i.



A horizontal jacketed drum is closed by stuffing-boxes at each end, and contains working paddles covered by gauze. A pump A draws hydrogen from a three-way valve B and passes it through C into the vessel. The vessel is one-fourth to one-fifth full of oil and catalyst. Unabsorbed hydrogen is blown off at D. The oil is run out at E. The temperature of hydrogenation is 150° C. to 160° C. Kieselghur is suggested as a carrier for the catalytic nickel. (United States Patent, 1,008,474, 1911.)

FIG. 20c.—Wilbuschewitsch Process for Hydrogenation of Oils. (See p. 100k.)



**Wilbuschewitsch Process** (see United States Patent, 1,079,278, 1913; also U.S. Patent, 1,024,758 of 1912; English Patents, 15,440, 1911; 72, 1912). The apparatus is shown in Fig. 29c, p. 100j.

The vessel *R* contains the fat to be treated, and the vessel *O* contains the catalyst. Pumps *AA'* feed the oil and catalyst into a mixing device *B*, by which an

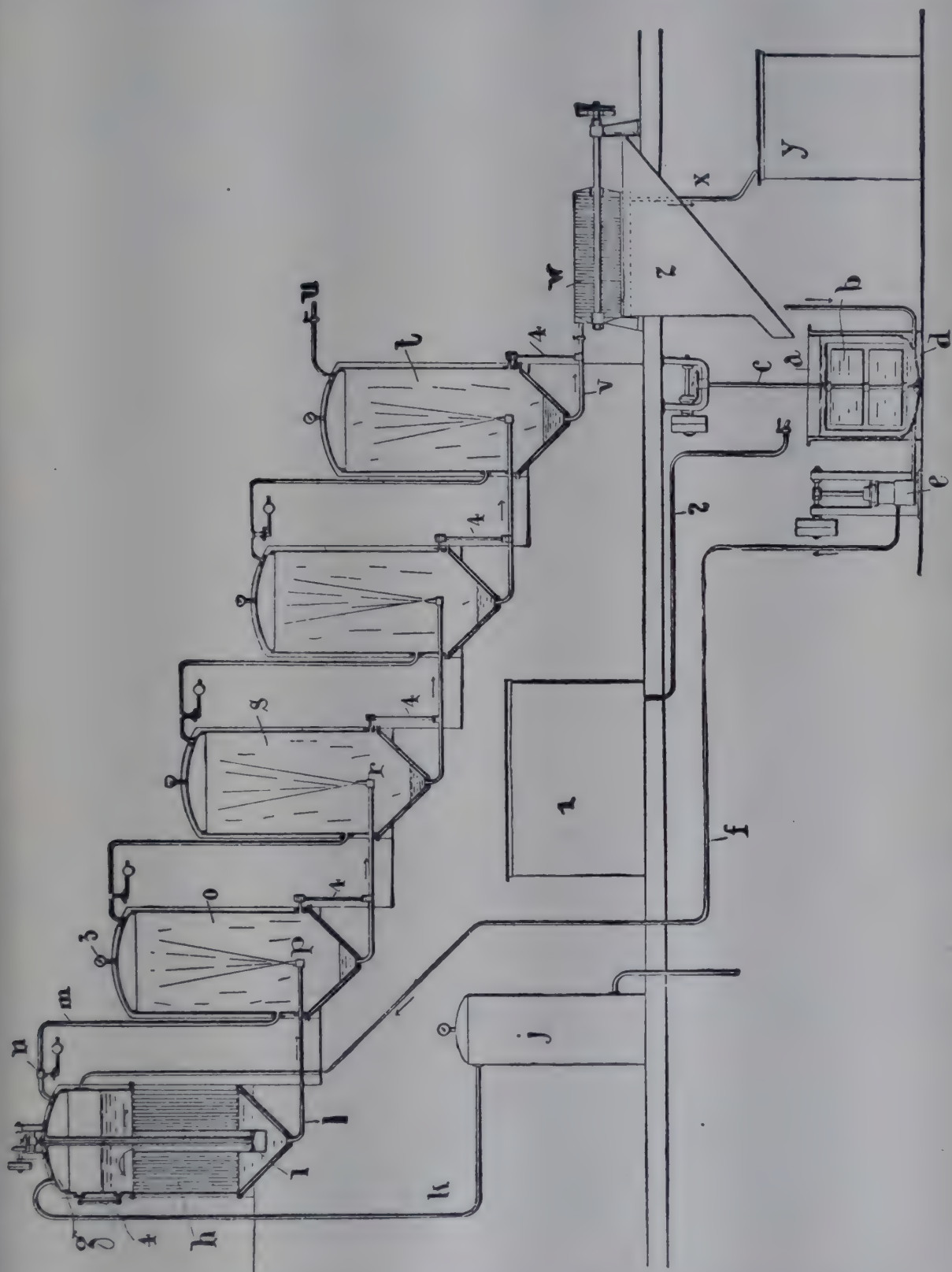


FIG. 29c.—Testrup's Process for Hydrogenation of Oil. (See p. 100l.)

intimate spray of catalyst and oil is obtained. The mixture passes through a pipe *G* and a valve *H* into an autoclave *J*, which is furnished with a spraying device *C*, which consists of a number of nozzles so arranged that the oil and catalyst are uniformly sprayed into the whole inner space of the autoclave. A compressor *K* forces hydrogen into the autoclave under a pressure of nine atmospheres, the hydrogen passes through a pipe *x*, which extends from the upper part of the

autoclave downward to its lower end, and terminates in an admission nozzle  $D_1$ . By this spraying system an intimate contact of oil and hydrogen on the counter-current principle takes place. The autoclave is heated to  $100^\circ$  to  $160^\circ$  C. The partially hydrogenated oil collects in the conical part of the autoclave, and is sprayed in the form of a fountain through the autoclave by the incoming hydrogen. The oil from the first autoclave  $J_1$  is forced by a pump  $E_1$  into the second autoclave  $J_2$ , the hydrogen entering through the pipe  $J_2$ , and the actions occurring in the first autoclave are repeated.

Several autoclaves can be arranged in series in this way. When the fat is sufficiently hardened (determined by withdrawing a sample and determining the melting point or iodine value) the oil and catalyst mixture is run out through the valve  $U$  into the centrifugal apparatus  $F$ , where the oil is separated from the catalyst. The clear oil runs into the tank  $N$ , while the catalyst passes through the pipe  $R_1$  and the valves  $S$  and  $T$  to the vessels  $O$  and  $P$ . Spent catalyst is run into the tank  $P$  to be regenerated. Fresh catalyst is introduced through the valve  $T$ . Unabsorbed hydrogen passes through the check valve  $W$  and the pipe  $Q$  and cooling worm  $L$  into a washing vessel  $M$  filled with caustic soda lye, where it is purified and passed on to the compressor and autoclaves.

**Testrup's Apparatus** (English Patent, 7,726, 1910) is also based on a spraying system. The apparatus is shown in Fig. 29f, p. 100k. It consists of a series of closed autoclaves  $g, o, s, t$ , in which oil and catalyst are sprayed in series into hydrogen gas at a continually decreasing pressure.

Thus in  $g$  the oil, heated to  $160^\circ$  to  $170^\circ$  C., is subjected to hydrogen at 15 atmospheres pressure. In  $o$  the hydrogen is at 12 atmospheres pressure. This difference in pressure causes the oil to spray from  $g$  into  $o$ .  $s$  has a hydrogen pressure of 9 atmospheres, and, consequently, oil sprays from  $o$  into  $s$ . The oil and catalyst are thus sprayed several times into gas at successive lower pressures. The oil enters by the pipe  $f$  and the hydrogen by  $k$ ;  $n$  is a reducing valve for regulating the pressure of the gas in the next autoclave;  $h$  shows heating tubes for superheated steam;  $l$  is the pipe carrying the oil to the spray nozzle  $p$ . The oil is pre-heated to  $160^\circ$  C. in the vessel  $a$  which is provided with stirring arms.  $i$  is the storage tank for the oil, while  $w$  is the filter press for removing catalyst from the treated oil;  $y$  is the treated oil tank.

It should be noted that both Wilbuschewitsch and Testrup's system refer to the "spraying" or "atomisation" of the oil into the hydrogen. A number of patents exist, the object of which is to bring the catalysts, oil, and hydrogen into intimate contact. Yet all that is apparently needed is a gentle mixing of the contents, as very rapid diffusion takes place.

**Ellis** (U.S. Patents, 1,026,156, 1912; 1,052,469, 1913; 1,040,531, 1912; also British Patents, 24,084, 1912; 16,782, 1913; 16,600, 1914) uses tubes filled with catalysing material in granular form, and allows the oil to flow through the tubes in one direction while passing the hydrogen in an opposite direction.

Fig. 29g, p. 100m, shows a vertical type of apparatus. The catalyser being shown at  $C$  in the tube  $A$ . Oil enters by the pipe  $O$  and passes into the tube or cylinder  $A$ . The pump  $P$  causes the oil to circulate from the top to the bottom of the apparatus through the pipe  $B$ . Hydrogen gas admitted at  $H$  is pumped to the bottom of the cylinder  $A$ , and the excess is withdrawn at the top by the pipe  $D$ , passing through the drier  $E$  and back into the treating cylinder. In another form of apparatus Ellis arranges the catalyser in beds or trays, instead of in a bed of considerable depth. See United States Patent, 1,040,531, 1912.

**Calvert** (English Patent, 18,350, 1913) mixes the oil and gas by means of a rotary stirrer driven by an electric motor contained in the autoclave itself, and under a hydrogen pressure equal to that at which the reaction is carried out.

**2. Wet Processes.**—In these processes the catalyser is generated in, and not without, the oil to be hardened. A compound of nickel is introduced into the oil (or part of the oil) to be hardened, and the whole is heated while a stream of hydrogen is passed through. The nickel is thus produced *in situ*.



Three processes have been worked on a large scale:—

1. **The Bedford-Erdmann Process** (see English Patents, 2,520, 1907; 29,612, 1910; 27,718, 1912; 28,981, 1912; United States Patent, 949,954, 1910; German Patents, 211,669, 1907; 221,890, 1909).—Nickel oxide is introduced into the oil, which is heated to  $255^{\circ}$ - $260^{\circ}$  C. Hydrogen gas is then passed through, which reduces the oxide to the metallic state with the liberation of water (see United States Patent, 1,026,339, 1912).

The disadvantage of the use of nickel oxide is the high temperature that it is necessary to employ in order to cause reduction, this temperature being close to the temperature of decomposition of the fat. A partially decomposed fat causes a bad colour and taste in the hydrogenated oil.

Erdmann introduced certain improvements into this process, producing the oxide by special processes. The oxide, for example, is produced from the nitrate instead of from the sulphate (see *Siefen. Ztg.*, 1913, 1413; also German Patent, 211,669, 1907).

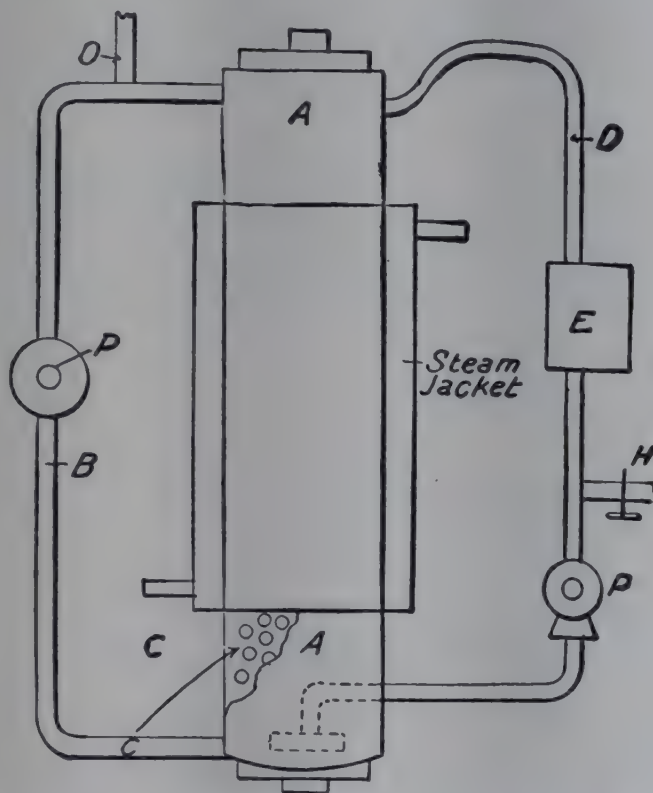


FIG. 29g.—Ellis's Process for Hydrogenation of Oil. (See p. 100f.)

A small factory was erected at Sleaford, England. A company, called the "Ardol Co., of Selby," is stated to be working the process. In Germany the "Ammendorfer Oelhartungswerke" is stated to have adopted the process.

2. **Wimmer-Higgins Process** (see English Patents, 25,326, 18,282, 1912; 23,377, 1912; 4,144, 1913; 4,665, 1914; also United States Patent, 1,081,182, 1913).—Here the nickel is introduced into the oil in the form of salts of organic acids like formic, oxalic, or lactic acids.

These salts are much more easily reducible than oxide of nickel, so that overheating is avoided.

It has been objected, however, that on heating carbon monoxide is split off (which acts as a catalytic poison), and that the organic acids are liberated, which attack the apparatus. In Germany a company to work the process has been formed called the "Fettrafinerie, A. G., Bremen und Brake."

3. **Process of the Norsk Hyderings Company** (see English Patent, 11,540, 1913; 11,543, 1913). In this process nickel carbonate is the salt of nickel employed, which is reduced in oil at a lower temperature than the oxide,



and is stated to be free from the defects of the Wimmer-Higgins process. The company hold Fuch's patents.

The process of reduction is thus described in Fuch's patent, No. 11 542, 1913 :—

"1,000 (one thousand) kilograms of castor oil are mixed with 1.2 per cent. of finely-powdered and freshly-prepared nickel carbonate previously dried at 110° C., and the mixture is then heated to 230° C., whilst a current of hydrogen is slowly allowed to pass through the same; as soon as this temperature of 230° C. is attained, highly-compressed hydrogen (say from 12 to 15 atmospheres) is admitted into the mixture through a capillary nozzle. The reduction of the salt to metallic nickel takes place under the well-known characteristic phenomena, namely, with slight frothing due to the formation of water. As soon as this operation is completed, the temperature is lowered, and the reduction of the oil carried out as an uninterrupted continuation of the preceding operation."

In a second patent of Fuch's, No. 11,543, 1913, held by the company, the following conditions are laid down for increasing the speed of the hydrogenation :—

"An essential increase of the speed of the reaction is obtained by maintaining the oils under treatment at a moderate temperature of from 90° to 150° C., while the reducing gas is heated to a higher temperature, namely, say from 200° to 250° C.

"The avoidance of a too high heating of the mass itself has a favourable influence upon the final product, whereas the heating of the reducing agent appears to produce an increase of its activity. Comparative experiments have shown that by these means the speed of the reaction can be increased to the extent of over 10 per cent.

"Care must be taken to increase the efficiency of the reducing gas by a preceding splitting of its molecules into atoms. This can be done by subjecting the gas to chemically active rays. A dissociation of the hydrogen also appears to take place when it is conveyed over catalytically acting substances, such, for example, as spongy platinum or freshly-prepared metallic nickel. The dissociated hydrogen possesses, as has been proved by comparative experiments, an increase of activity of from 15 to 20 per cent. The catalytic substance can be located within a suitably long pipe or upon trays of a column apparatus, and the necessary heating may be effected by way of example by means of a heated oil casing."

This process is worked on a very large scale by the following companies :—

**Norway.**—The Vera Fedtraffineri A.S., Sandefjord. Capacity, 16,000 tons per year. Edible and industrial fats.

**Sweden.**—Aktiebolaget Henriksborgs Fabriker, Stockholm. Capacity, 10,000 tons per year. For hardening vegetable oils for industrial and edible hard fats.

**Denmark.**—A.S. Oliehaerdningsfabriken, Kjobenhavn. Capacity, 8,000 tons. Edible fats from Soja bean oil.

**Holland.**—Jan Dekker, Wormerver. Capacity, 4,000 tons.

**Belgium.**—De Bruyn, Ltd., Termonde. 10,000 tons. Edible fats.

**France.**—Societe de Stearinerie et Savonnerie de Lyon. 8,000 tons. For candle and soap manufacture.

**Italy.**—"Corisoleum" Societa Italiana per l'Industria degli Olii, Mira. 16,000 tons. For candles, soaps, and edible fats.

**Germany.**—Centra A.G., Krischwitz Elbe. 20,000 tons for candles, soaps, and edible fats.

**Roumania.**—Phenix Societate Anonima Romana, Bucharest. 4,000 tons for edible fats.

(3) **Gaseous Processes.**—In these the nickel is passed into the oil in the form of an unstable gaseous compound, namely, nickel carbonyl.

This is decomposed in the oil, depositing the nickel, and liberating the carbon monoxide.

**Shukoff** (see German Patent, 241,823, Jan. 18, 1910. Also H. Kamps, Belgian Patent, 246,975. United States Patents, 738,303, 777,848, 943,627) seems to have been the first to have claimed the process of hydrogenating oils by means of nickel derived from the decomposition of nickel carbonyl.

The carbonyl is obtained from reduced nickel by passing carbon monoxide over it at a low temperature. The carbonyl is soluble in oil, and when the solution is heated to 200° C., the nickel is set free and can be used as a catalyser.

It is stated by some authorities, however, that the carbon monoxide acts as a catalytic poison for the nickel.

**Lessing** (British Patent, 18,998, 1912) has worked out a process for the hydrogenation of oils by the use of nickel carbonyl, and a company has been formed to work it, namely, the Hydronyl Syndicate, Ltd., 140 Leadenhall Street, London.

The system is worked on the counter current principle. A gas composed of hydrogen and a small amount of carbon monoxide is passed over nickel contained



in a container and heated to a suitable temperature. The carbon monoxide takes up the nickel, and the gas then passes into the heated oil. The nickel carbonyl decomposes in the oil, setting free the nickel in a nascent condition. The hydrogen present then acts in the presence of this catalytic nickel, and hydrogenises the oil. The presence of carbon monoxide is stated not to poison the nickel to such an extent as to stop the rapid action of the nickel, because the nickel is liberated in an atomic condition, and acts so rapidly in this condition in the presence of excess of hydrogen that the poisoning or slowing effect of the carbon monoxide on the nickel does not have practical results.

In Lessing's process only ordinary atmospheric pressures need be used, and a temperature of from 160°-200° C. is required to decompose the nickel carbonyl passing through the oil. A maximum amount of 0.1 per cent. metallic nickel is used. The nickel may be recovered from the oil either by filter-pressing or centrifuging in suitable apparatus.

In the ordinary processes of oil hardening the nickel catalyst must be recovered by dissolving in sulphuric acid (or other acid), making into nickel sulphate (or other suitable salt), then precipitating as carbonate and reducing again. In the Lessing process, however, this procedure is avoided by returning the spent nickel catalyst into a heated cylinder, and passing carbon monoxide over it. The carbon monoxide picks up the nickel, and the nickel containing gases passes once more into the heated oil. The process can be worked continuously, oil travelling in one direction and the gases in the other. The carbon monoxide can be recovered and used over and over again.

**Uses of Hardened Fats.**—The process of hardening fats has now become of great industrial importance, because so much of the natural supply of hard fats is now employed in the making of margarine and other foodstuffs that the amount of such fats available for soap-boiling and candle-making has seriously diminished.

Hydrogenated and hardened fats are at present used largely for **soap-making** (see English Patent, 13,042, 1907.) Although the soaps produced are hard and do not lather well, this difficulty could be got over by mixing the hardened fat with a suitable amount of another fat which would give the necessary qualities to the soap.

The soap made from hardened fat is stated to give satisfactory results with a much larger percentage of resin than can be used in soap made from tallow or palm oil.

By subjecting fish oils and other unsaturated glycerides to hydrogenation, their unpleasant smell is completely removed, and this makes the process particularly valuable, this de-odorising effect, however, is only obtained if the hydrogenation is carried out nearly to completion.

Hardened **fish oils** must have their iodine value reduced to under 50 if they are to yield a suitable washing soap, devoid of all smell of fish oil.

Consequently, it is not possible to de-odorise an oil by this process without hardening it, so that the process has little value for the makers of soft soap and others users of liquid oils.

Hardened **cotton-seed oil** and hardened **whale oil** are used for edible purposes, and recently the use of hardened fats in this respect has greatly increased. They form excellent frying fats, and are now used in increasing quantities in the manufacture of margarine.

No difference between the digestibility of hardened fats as compared to those of natural fats has been found. Obviously, a hardened edible fat should melt below the temperature of the body in order to obviate indigestibility.

Hardened fats differ from natural fats in that they appear to be more easily saponified by alkalies. Leimdorfer (*Sciensieder Ztg.*, 1913, 40, 1317) suggests that hardened "stearin" is an allotropic modification of the natural glyceride.

Hardened oils are stated to have been used in the manufacture of chocolate instead of the expensive cocoa butter. They have also been used for lubricating purposes. In the tanning industry stearin, produced by hydrogenation, has been employed instead of oleo-stearin.

**Nickel in Hardened Fats.**—An oil hardened by a process, which includes Ni as a catalyst, may contain 0.5 to 2 mg. Ni per kilo., and possibly deleterious effects might arise from the unlimited consumption of such oil. Normann



and Hügel (*Halbmonatsschrift für Margarinindustrie*, 1913, VI., No. 17) showed that this quantity of Ni is often contained in foodstuffs prepared in nickel vessels, which have had no injurious effects on persons who have consumed them. Feeding trials with commercially hardened oils containing from 0.07 to 6 mg. of nickel per kilo. have been carried out without ill effects ensuing (see *Lehmann Chem. Zeit.*, 1914, 38, 798).

Prall has found that Nickel is found in fats only in *traces*, and then only when the oils used contain considerable amounts of *free acid*.

Sesame oil with 2.58 per cent. acid gave a hardened oil with 0.006 per cent. nickel oxide ( $\text{Ni}_2\text{O}_3$ ); a whale oil with 0.61 per cent. free acid contained 0.0045 nickel oxide in the hardened fat; with only 0.2 per cent. free acid in the original oil, no nickel could be detected in the hardened product. Bower states neutral oils do not take up nickel (*Z. Nähr. w. Genussm.*, 1912, 104).

**Testing for Hardened Oils.**—The only reliable test is the presence of nickel in the oils.

To detect nickel, 5-10 gms. of fat (still better 2½ lbs. [1 kilo.] in cases where the amount of nickel is very small) are warmed half an hour on a water bath, with an equal volume of concentrated, hydrochloric acid, shaking frequently; after filtering through a moistened filter, the filtrate is evaporated in a porcelain dish.

The residue gives (*Fortin Chem. Ztg.*, 36, 1,461 (1912)), when nickel is present, on touching with a drop of 1 per cent. alcoholic dimethyl glyoxime solution, a red coloration, which becomes more pronounced when ammonia solution is added. If the acid extract is itself coloured, it must be boiled with animal charcoal, and filtered.

**Kerr** (*J. Ind. and Eng. Chem.*, 1914, 207) ashes 10-20 gms. of hardened fat, dissolves the ash in HCl, evaporates to dryness, and ignites to free from organic matter, transfers to a tall 50 c.c. cylinder, and moistens with a few c.c. of distilled water. Then 50 c.c. of standard dimethyl glyoxime (5 gms. dissolved in 50 c.c. absolute alcohol, and made up to 100 c.c. with concentrated aqueous ammonia, and kept in well-stoppered bottle) are added. The presence of nickel is shown by a red coloration or precipitate. The tint is compared with that produced under same conditions with a nickel solution of known strength.

Edible fat must not contain more than 0.05 mg. of nickel per kilo.

The introduction of hardened fats has rendered doubtful of interpretation many of the standard tests used for specific oils.

The following points are of importance in this connection:—

1. **The Iodine Value.**—This is the most important value, as it gives the degree of hydrogenation of the oils. For methods of carrying out, see under *Analysis of Oils*.

2. The distinctive aromatic alcohols, *Phytosterol* and *Cholesterol*, are *unaffected by hydrogenation*, so that after hydrogenation it is still possible to ascertain whether an oil is of animal or vegetable origin. (See under *Analysis of Oils*.)

3. Most of the tests for individual oils are destroyed, because the process of hydrogenation destroys the substances giving rise to these tests. Thus the *Baudouin Test* for *Sesamé Oil* (red colour when oil is shaken with cold hydrochloric acid and sugar) is rendered almost useless. The same applies to the *Halphen Test* for *Cottonseed Oil* (orange-red coloration when oil is heated with an equal volume of amyl alcohol and carbon disulphide (1 : 1), the latter containing 1 per cent. free sulphur). The test is rendered more sensitive if *pyridine* is substituted for amyl alcohol, and a closed tube used for the test. (See Gastaldi, *Chem. Zeit.* 1912, 2, 758.)

3. **Hardened Fish Oils and Whale Oil** are said to contain arachidic and behenic acids—which are the characteristic acids of *Arachis Oil*. Hence an oil adulterated with hydrogenated fish oils would be difficult to distinguish from *Arachis Oil* by the *Bellier Test* (fractionating the lead salts of the fatty acids by treating with 70 per cent. alcohol).

4. The process of hydrogenation does not effect to any great extent the *saponification value* of the oils thus treated. The *Acetyl value*, however, is usually lowered, owing to the splitting off of hydroxyl groups (Normann and Hügel, *Chem. Zeit.*, 1913, 37,815). Thus it would be difficult to detect castor oil when fully hydrogenated by the saponification value and acetyl value.



## X.—SOAP—MODERN MANUFACTURE AND ANALYSIS

BY G. MARTIN, Ph.D., D.Sc.

REVISED BY E. I. COOKE, M.A., B.Sc., A.R.I.C.

### LITERATURE

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 LEWKOWITSCH, “Oils, Fats, and Waxes,” and WRIGHT and MITCHELL, “Oils, Fats, and Waxes,” give excellent summaries of soap-making.

Soaps are the metallic salts of fatty acids. The sodium and potassium salts of the fatty acids are soluble in water and constitute our ordinary “hard” and “soft” washing soaps respectively—although to-day certain sodium salts are manufactured which are quite soft, while certain potassium soaps possess a considerable degree of hardness, so that the old distinction between these classes of soap no longer holds accurately.

The soaps of other metals, *e.g.*, calcium, aluminium, magnesium, etc., are all insoluble in water, and so are quite useless for detergent purposes. Aluminium soaps (made by adding saponified linseed or cotton-seed oil to a solution of alum) are, however, used to impregnate waterproof material and to thicken oils; while lead and manganese soaps are used in varnish making (which see).

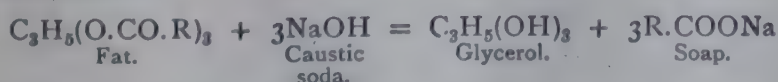
We may classify the processes employed in soap manufacture under three heads:—

1. *Soap-making processes where glycerol is set free and separated from the resulting soap.*
2. *Soap-making processes where glycerol is set free, but is not separated from the resulting soap.*
3. *Direct neutralisation of fatty acids with alkalis, no glycerol being produced.*

We will consider each in turn.

### Soap-making Processes where Glycerol is set free and separated from the resulting Soap

When the natural oils or fats are boiled with caustic soda they are decomposed according to the equation:—



The glycerol is recovered from the liquid which settles out below the soap.

This is the process employed on the largest scale at the present time. Measured

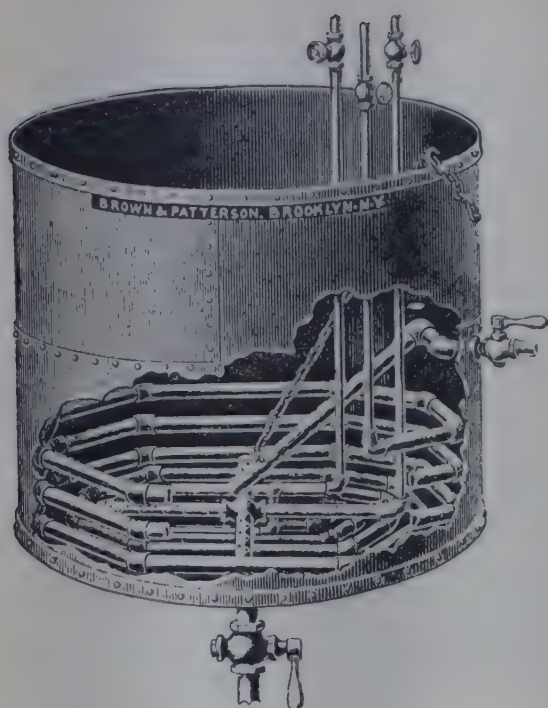


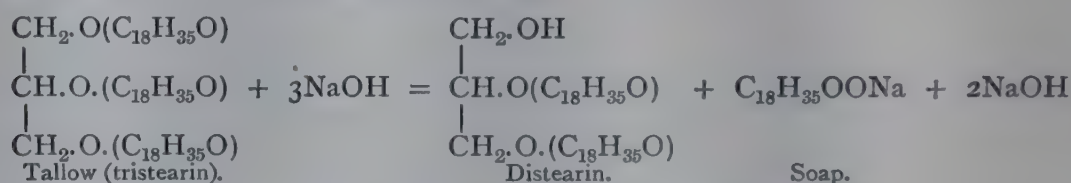
FIG. 30.—Soap Kettle, showing closed and open steam pipes, swivel-joint outlet pipe, and outlet valve.  
(Brown & Patterson, New York.)

amounts of oils and fats are run into a large cylindrical vessel, called a soap kettle, varying in diameter from 5-25 ft., and in depth from 8-30 ft., and fitted with an open steam coil for heating the contents, and a 3-in. outlet valve at the bottom for running off the lye. At the side is an outlet pipe of 3-4 in. diameter connected with a swing joint and a 3-in. cock, for transferring soap to the mixer or "Crutcher."

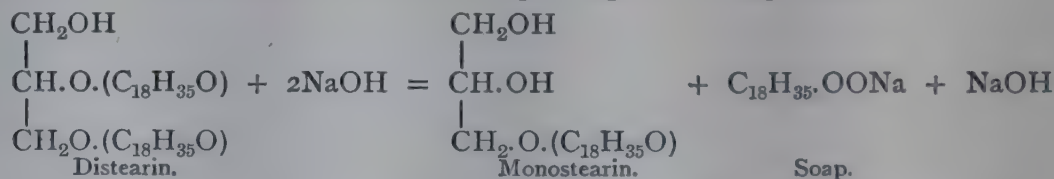
The proper amount of oil having been introduced, a dilute solution of caustic soda "lye" of 15° Be. is run in from the lye tank, steam is turned on, and the whole is vigorously boiled. As the caustic soda is taken up by the fat, more and more is added, care being taken, however, not to add it too quickly, for if present in excess it will retard the saponification. An excess of caustic soda, however, is required for the completion of the saponification.

The saponification takes place in three stages.

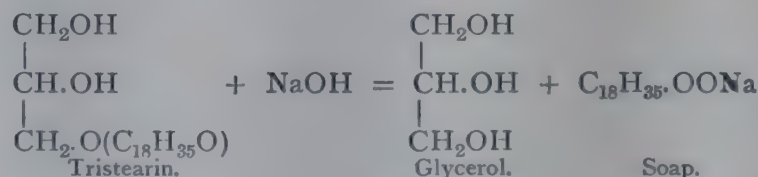
First an emulsion is formed, owing to the change:—



Next a pasty mass is produced when the change has gone one stage further:—



Finally a clear homogeneous mass appears in the kettle, which represents the complete saponification:—



In the clear mass there is present at this stage: soap, glycerol, some caustic soda in excess, some salt, sodium carbonate and sulphate (impurities in the caustic soda), and any unchanged animal tissue present in the fat. If saponification has been properly completed there should be no free or unsaponified fat.

Dry salt is now shovelled into the mass and scattered over the surface (see p. 121*a*). Soap is but feebly soluble in a solution of brine, and so it separates out into a layer of soap above and glycerol water and excess lye below. The process is known as "graining" or "cutting" the soap.

A tallow or cotton-seed soap stock will be satisfactorily grained with 7-19 per cent. of salt in the stock lye. Cocoa-nut oil soap requires much more.

After each addition of salt the mass is well boiled up in the kettle, and the appearance of the soap noted. As water is withdrawn from the soap to dissolve the dry salt it loses its transparency and assumes a "grain-like" appearance. Finally



the neutral lye separates out below and the soap above. The addition of salt is now discontinued, and the contents of the kettle well boiled in order to intimately mix the lye.

Finally steam is turned off, and the lye allowed to settle out. The time required for this depends upon the size of the soap kettle. Sometimes two hours are sufficient, but usually the whole day is taken up in saponifying, and the lye allowed to separate overnight. The neutral lye is then run off at the bottom of the soap kettle, and is either pumped to the glycerol refinery, or stored until convenient for using. The curdy soap remaining in the kettle is again boiled up with water to form a homogeneous paste ("closed"), a strengthening charge of caustic soda is added, and the boiling continued, to ensure complete saponification, and at the same time to wash out impurity from the soap, for much colour is discharged into the alkaline lye. Finally, the lye is again separated by graining with salt as above described. This is known as the "pickle change."

Sometimes the soap is again treated in the same manner in order to remove impurities which spoil its colour—the impurities being discharged each time with the lye.

If the soap is to contain rosin, the "strengthening charge" of caustic soda is omitted and the rosin is added after withdrawing the second lot of lye. The rosin is added in fragments smaller than a man's hand, live steam being passed simultaneously through the grained soap. If added by hand, the addition of rosin continues over several hours, during which time only sufficient steam is needed to keep the soap hot and slowly melt the rosin. When all the rosin is added a considerable amount of lye at 20° Be. is run in and the mass vigorously boiled. Rapid combination ensues, and lye is added as required in order to prevent the soap from "closing" (*i.e.*, forming a homogeneous mass with the lye). Indeed, the soap must be kept "open" (*i.e.*, separated in a distinct layer from the lye) by the addition, if necessary, of more 20° Be. lye, and when no more of this is absorbed, with dry salt. With the soap "open" (separated from the lye) combination with alkali with rosin (an acid body) takes place rapidly, and an easy discharge of colouring matter into the waste lye beneath occurs. When the change is completed the highly coloured and impure lye (which contains practically no glycerol since this has been removed with the lye of the two previous operations) is run away down the sewer. Then sufficient water is added, with boiling, so as to just "close" the soap (*i.e.*, make it into a homogeneous paste with the lye), and then a strengthening charge of 20° Be. is added, with boiling, until the soap is again "opened" (*i.e.*, separated as a layer from the lye), the lye being added as fast as it is absorbed.

When the absorption ceases, the saponification is completed, and the whole is boiled. If the soap tends to "close," brine from 10° Be. to 20° Be. (according as the soap is thick or thin) is added. The lye separating should be alkaline ("strength lye"). After turning off steam the lye is allowed to settle out overnight, withdrawn, and (since it contains free caustic soda) used for treating another lot of stock, or added to the grained nigre or stock change of other boilings, where it assists in the saponification of fresh stock.

The soap must now be "fitted," *i.e.*, brought to the condition of finished soap. To do this, the strengthening lye is withdrawn if it has been used, and the open soap is boiled up with water until the whole forms a homogeneous paste. Additions of water are now made very carefully, each addition of water being followed by a thorough boiling, and its effect noticed. The art of the soapmaker consists in so adjusting operations that the soap contains just the proper amount of water, and yet is still "open" enough to allow the intermingled aqueous solution and impurities (principally iron salts of fatty acids) to settle out.

Addition of water should cease when the soap boils up regularly with but little steam, and rolls over a stiff surface, breaking into saucer-like depressions which retain their firmness and transparency from the centre to the circumference of the kettle. Much experience is required to produce the proper degree of hydration.

Soft-bodied stock (grease, cotton-seed oil, heavily rosined tallow) and firm stock (tallow and cocoa-nut oil) for unfilled soaps such as Castile, floating soap, and milled soap base, require but little water, whereas soap intended to be filled with soda-ash solution, or tallow soap slightly rosined, require much water.

If the soap is to be quite neutral, a little cocoa-nut oil may be added towards the close and well boiled through. This effectively neutralises the free alkali, and greatly improves the finished soap. Sometimes "oleic acid" (red oil) or melted stearic acid is added for the same purpose.

When brought to the proper degree of hydration, the mass is allowed to settle for some days, when there is found at the bottom of the pan a very small amount



of alkaline solution, above which rests a layer of dark soap called "nigre," and above this rests the bulk of the finished soap ("neat soap"), covered on the top by a thin layer of solidified soap in a spongy condition, owing to air bubbles

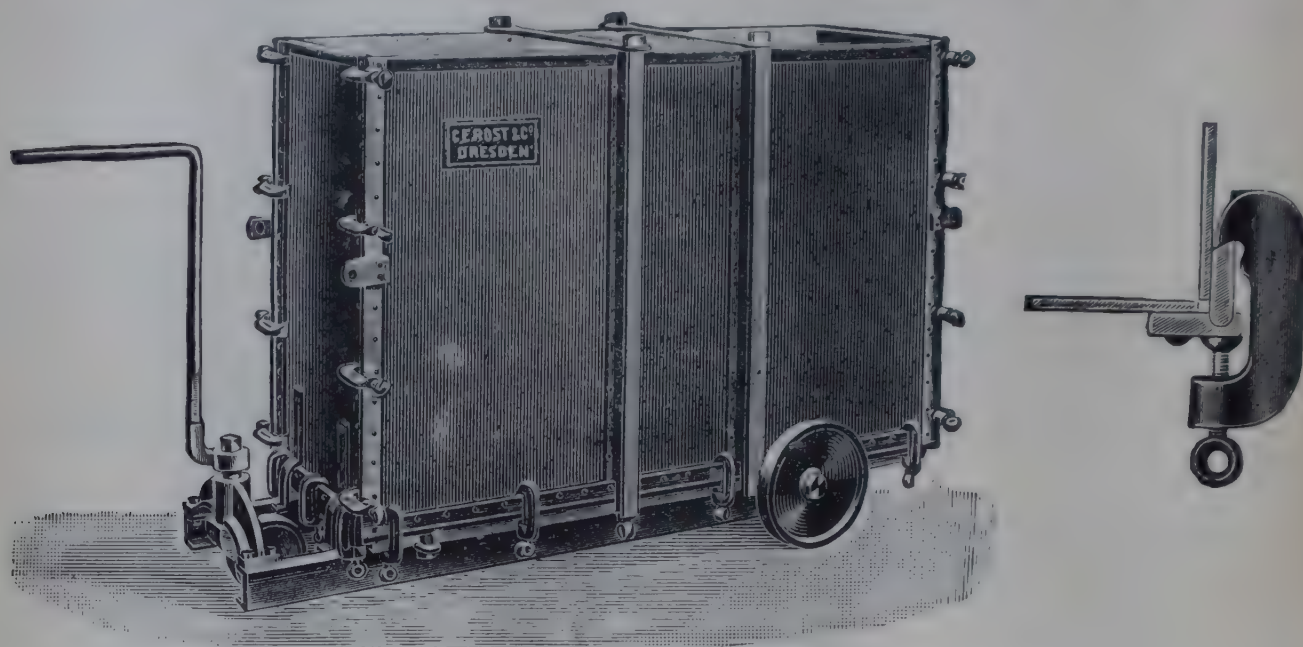


FIG. 31.—Soap Frame, with Clamp. (Rost & Co., Dresden.)

which have risen from below during the settling process. The "nigre" owes its dark colour to metallic soaps—usually iron ones—and contains caustic soda and excess of salt. Its volume varies between 25-35 per cent. of the mass. The

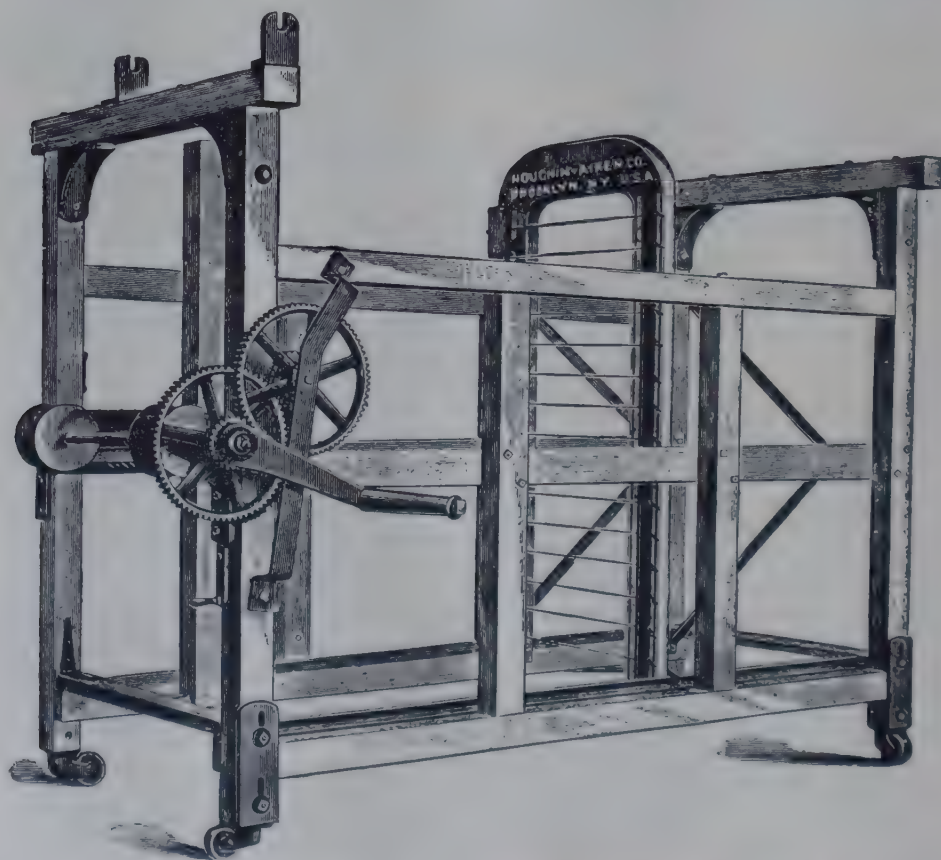


FIG. 32.—Soap Slabber. (Houchin-Aiken, New York.)

"neat" soap above the nigre should be practically neutral. The line of demarcation between the good soap and nigre is sharply defined.

If the soap is to be used pure, the "neat" soap is run directly whilst warm into



soap frames. These are iron plate boxes on a wooden base mounted on wheels, with detachable sides, and capable of holding from 12-15 cwt. of soap.

In some cases frames are made as high as 72 in.; the reasons for this are obvious. There are tops and bottoms in every case, and whether the frame is 30 in. or 72 in. high, the tops and bottoms are exactly the same thickness, and consequently much more remelting has to be done for the amount of soap turned out from a low frame than from a high one.

On cooling, the soap in the frame hardens and solidifies; the iron sides are then detached and the solid block of soap cut first into slabs either by a workman drawing a pianoforte wire through the block at intervals, or, more rapidly, by means of a machine called a "slabber."

When slabs of uniform thickness are required, a slabber such as that illustrated is usually used. But where slabs of various thicknesses are required, either a simple pianoforte wire, or still better, a hand machine, is used for cutting one slab at a time.

The slabs of soap are then cut into bars by placing in another machine in which a number of parallel wires attached to a movable frame are forced simultaneously through the slabbed soap, thus cutting it into pieces usually weighing 3 lbs.

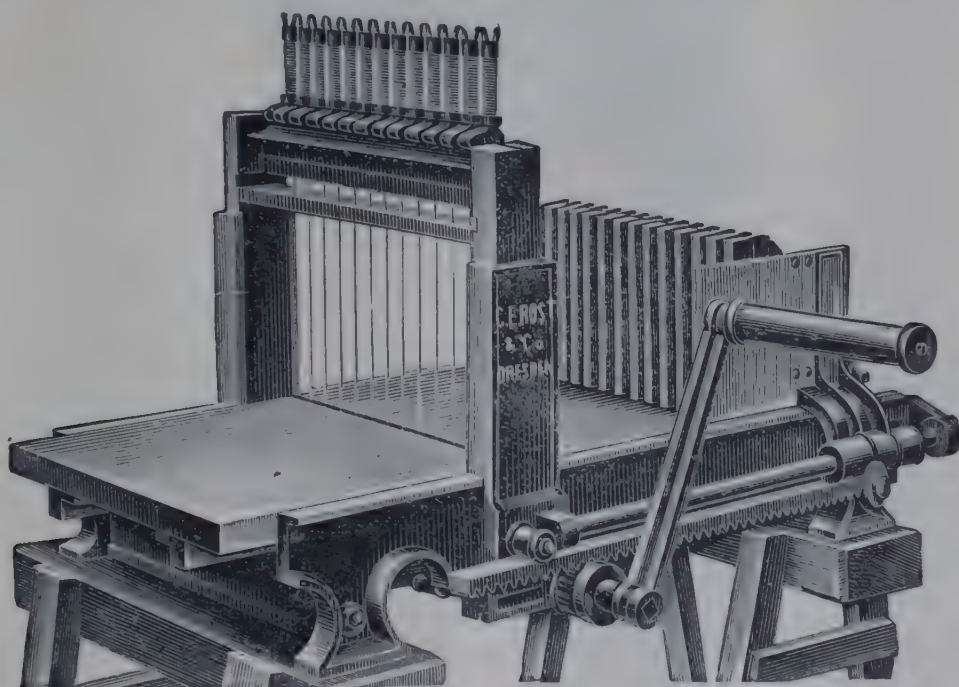


FIG. 322.—Bar-Cutting Machine. (Rost & Co., Dresden.)

Sometimes the bars of soap thus produced are stamped into cakes in special presses. This is always done with toilet soaps (which see). Fig. 35, p. 111, shows a typical hand press.

If, however, the soap is intended to be "*filled*," i.e., mixed with excess of sodium carbonate solution or with sodium silicate—substances much used in producing the cheaper sorts of soap, and having themselves considerable detergent qualities—or if perfumes and colouring matters are to be mixed with the soap, then the soap is first run into a mixing machine (called a "crutcher") and is there incorporated with the necessary materials by means of mechanical stirrers or screws (Fig. 33). After "crutching" for a sufficient time (sometimes with artificial heating in a steam jacket with which most crutchers are provided), the soap is finally run out into frames placed below the crutcher, and then the framed soap is cooled into blocks, slabbed, and the slabs cut into smaller pieces in cutting machines as previously described.

Since these frames, when filled with soap, often weigh considerably over half a ton, the floor of the factory should be of iron plate  $\frac{3}{8}$  to  $\frac{1}{2}$  in. thick, in order to avoid splintering the woodwork, and to facilitate the running of the heavy frames from one part of the works to another. Concrete floors are not advisable as they soon break up. Fig. 34 shows a conventional view of a soap factory.



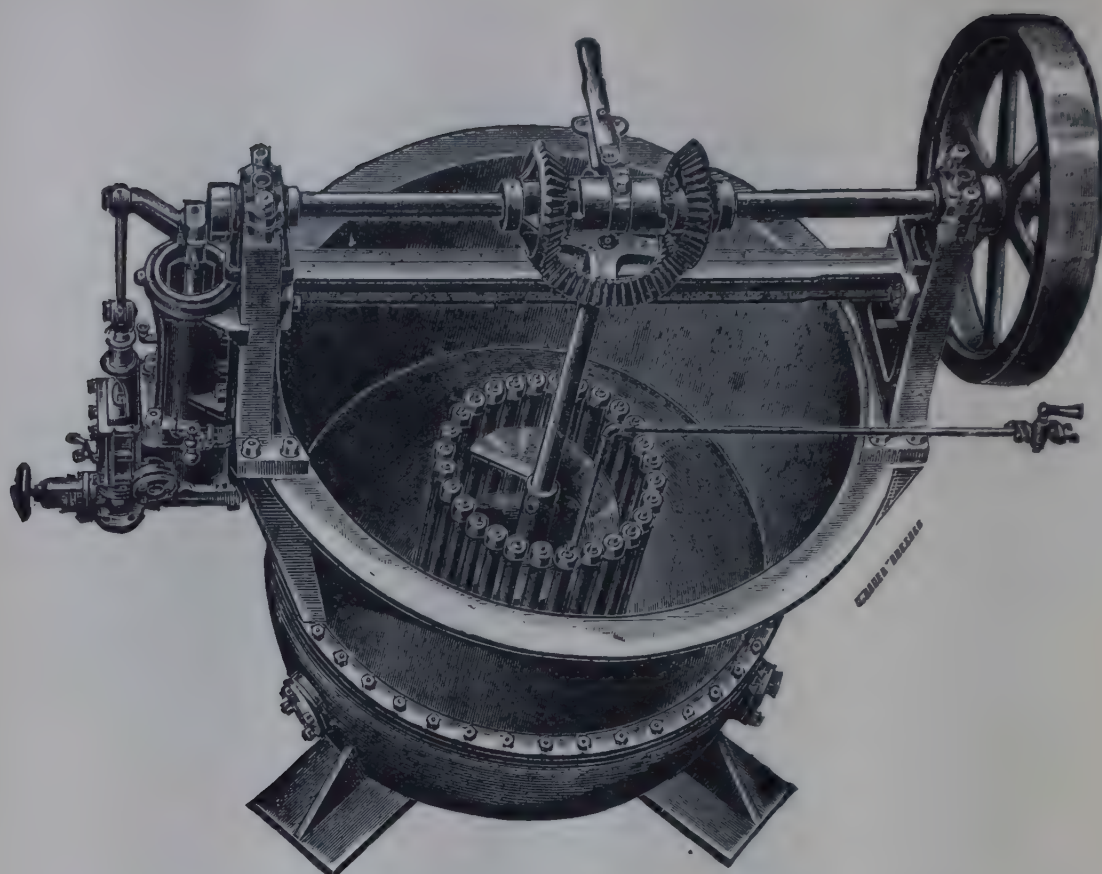


FIG. 33.—Soap Crutcher, showing steam-heating pipes and mixing screw.

The “nigre” or impure soap remaining behind in the soap kettle after the “neat” soap is run off is boiled up with steam and grained by throwing in dry salt and boiling. On settling, the lye underneath is run into the sewer while the nigre is utilised for adding to other soap stock, or used as a base for milled soap or floating soap.

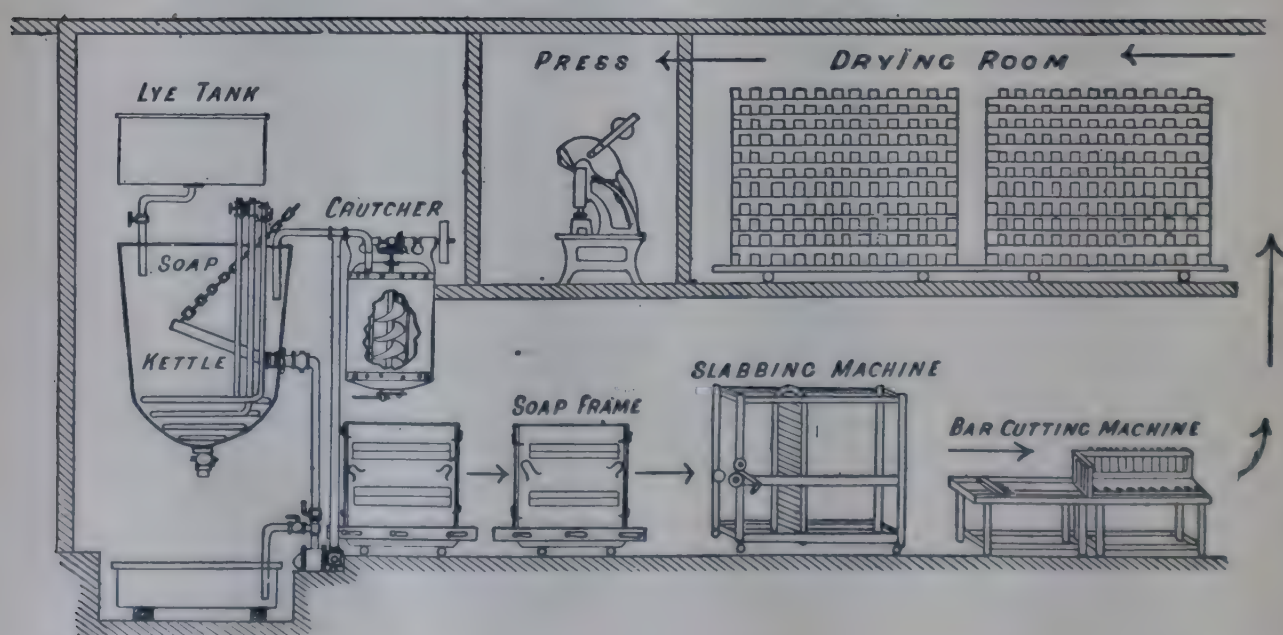


FIG. 34.—Conventional View of a Soap Factory, showing the course of manufacture from the Soap Kettle to the Pressed Tablet.





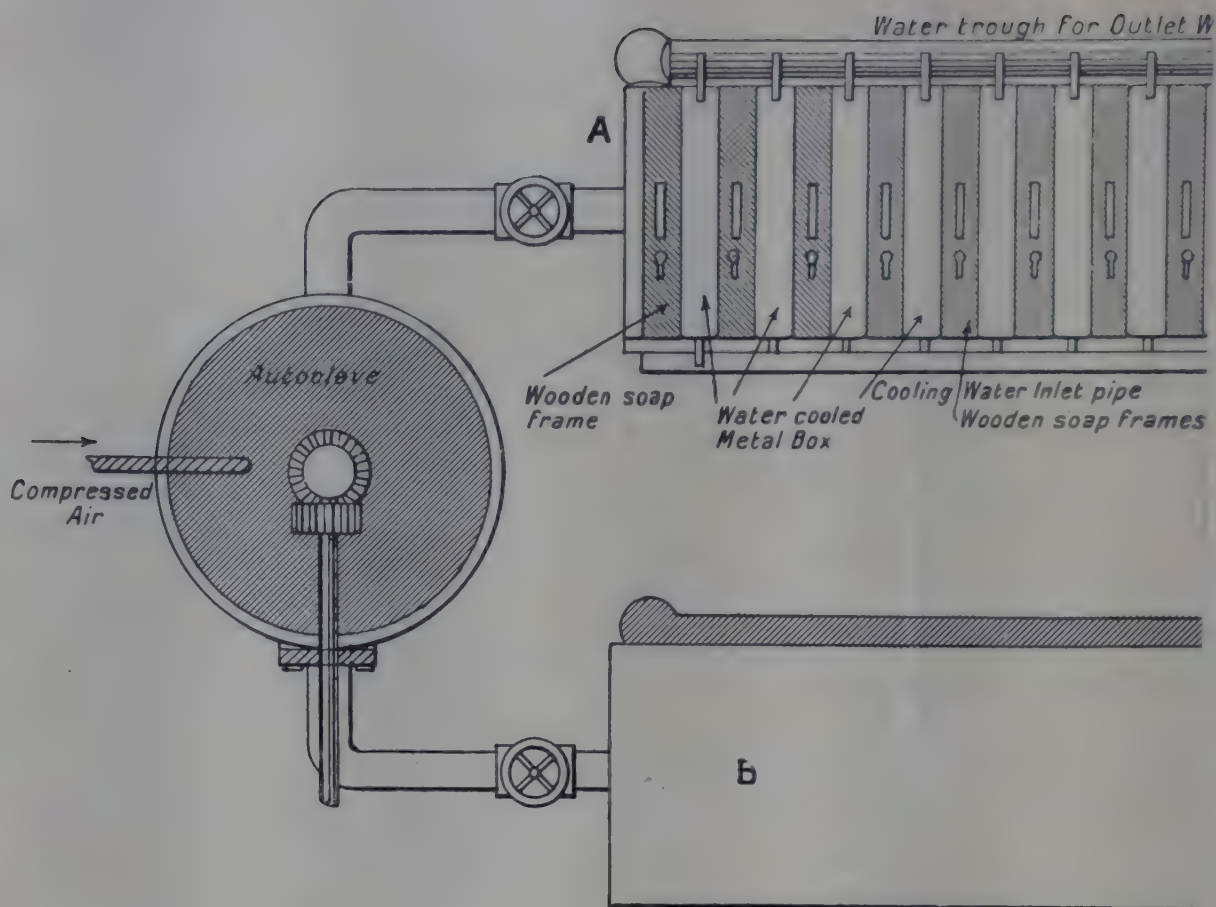


FIG. 34a. — Plan from above of Soap-Cooling system.

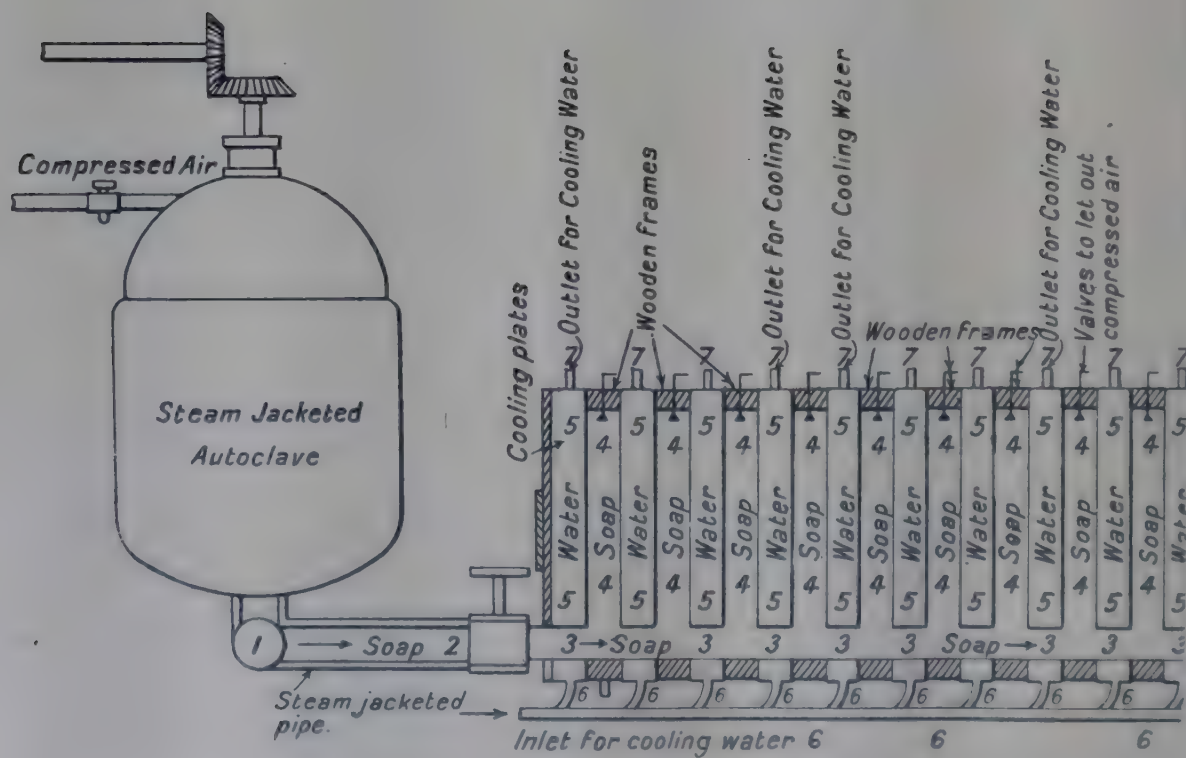


FIG. 34b. — Section (diagrammatic) of Soap-Cooling system.



## Replacement of Soap Frames by Soap-Cooling Machines

The great disadvantage of soap frames is that four or five days must elapse before the soap is cooled sufficiently to be cut up into bars. Also, they occupy a very large space in the factory. Machines are now on the market whereby two tons of soap may be run at once into special cooling machines, and the soap cooled by a stream of running water within one to one and a half hours. So that a pair of these machines working alternately will, in a working day of twelve hours, produce forty-eight tons of solid soap in a condition to be cut into bars.

In some of these special machines the soap is run into metal tubes surrounded by cold water (much like the candle-making machines). The core of cold soap is then forced out of the tubes by means of a piston. One of the most successful soap-cooling machines is made in the form of a filter press. Fig. 34*a* shows the general plan of such a machine, viewed from above. The liquid soap is run from the soap kettle into a steam-jacketed autoclave *C*, which is provided with stirring arms whereby ingredients can be mixed in with the soap. By means of compressed air the hot liquid soap is forced alternately out into either the soap-cooling machines *A* or *B*, which are so arranged that the one machine is being prepared for filling while the contents of the other are cooling, so that the process is nearly continuous. Each of the machines *A* and *B* will hold two tons of liquid soap, and the time of cooling varies from one hour in winter to two hours in summer. The structure of the machine is apparent from Fig. 34*b*—5, 5, 5 are nickel plated flat iron boxes through which a stream of cold water pours, entering at the bottom through the pipe 6, and pouring away at the top through the pipes 7, into a water trough. Figs. 34*c* and 34*d* show the arrangement of these cooling boxes in detail. Each box has a hole at the base through which the soap can flow, the holes forming a passage 3 (Fig. 34*b*) when the machine is connected up. The cooling boxes are mounted on strong iron rails, and move along on rollers. Also they are connected together by an iron band at the base, with slots cut in it, so that they have a certain play of movement. Between the cooling plates are wooden frames, shown in greater detail in Fig. 34*e*. These frames are covered inside with nickelled iron, and are clamped firmly together between the cooling frames, as shown in Fig. 34*b* and in Fig. 34*f*. The cooling boxes and frames are squeezed together by means of an electrically driven screw 8 (Figs. 34*a* and 34*b*). The screw is straightened by means of an electrical motor contained in the box 10. There is an automatic cut-off when the plates are pressed sufficiently together, the final tightening being made by the hand spokes 9. The hot liquid soap flows from the autoclave *c* (Fig. 34*b*), along the passage 1 and 2 into the space 3 in the cooling boxes, and then rises up in each compartment 4, being trapped by the wooden frames at the top, and the cooling boxes 5 at the sides. The air escapes through the outlet valves, which are inserted in the wooden frames (Fig. 34*g*). Each machine cannot be over-filled with soap, because the autoclave *c* has the same capacity as each soap-cooling machine. Very little soap leakage occurs, because the wooden frames squeeze up tightly against the metal cooling boxes, much in the same manner as the plates in a filter press. The soap solidifies as a solid block in the wooden frames. The motor is then started to reverse the screw and separate the plates. The wooden frames containing the slab of solid soap are lifted out of the machine, the block of soap is thrown upon a truck and carted off to the bar cutting machine. These soap-cooling machines are now displacing soap frames in most modern soap factories.

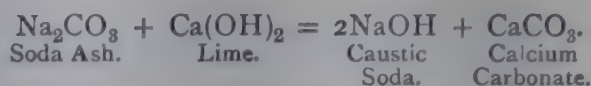
## Causticising Tank used in Soap Works

The apparatus is shown in Fig. 34*h*.

In order to turn soda ash into caustic soda, the lime is broken into lumps, and placed in the iron grids *A*, *A*, *A*. Sacks of soda ash are then thrown into the tank *MM*. Water (or weak caustic soda washings from previous batches) is then run into the tank, and the agitators *N*, *N*, *N*



started. Live steam is blown in through the pipe PP in order to heat the liquid. The following changes take place :—



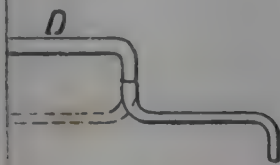
The caustic soda solution (6-7 per cent.) is run out through the skimmer BB, and is pumped by means of the pump C, through the pipe DD, into the caustic soda settling tanks E, E'. The calcium carbonate sludge left in the tank MM is stirred up three times in succession with water, and the weak caustic soda washings are pumped up to tank FF, when they can be used instead of water in tank A for a fresh charge, or can be pumped up to the lye tank on roof of soap works, and used as lye. The caustic soda solution in the tanks E, E' (6-7 per cent. NaOH) is run off to an evaporator and concentrated to 20-22 per cent. NaOH, when the liquors are stored for use in the soap kettle. The calcium carbonate sludge may be burned again for lime, or sold for cement, but most soap makers prefer to dump it. The tank MM is often used direct for dissolving caustic soda. The solid caustic soda is knocked out from the iron drums in which it is placed on the market, and placed in the grids A, A, A, and then dissolved in water by starting the agitators N, N, N. All these tanks are of sheet iron.

### General Scheme for Modern Soap Factories

Diagram 34 shows a small factory. A more detailed diagram is Fig. 34', which shows modern practice. The oil or tallow in casks 1 and 2 is run through openings in the floor A, B (covered with grids 3 and 4, to catch large objects), into the oil tanks 5 and 6 below. These oil tanks are fitted with closed steam coils 7 and 8 to keep the oil melted. If the oil in the cask has solidified (*e.g.*, palm oil sometimes is solid, also tallow and hard fats), the casks are steamed out, a steam pipe being used for the purpose, which is fitted on to a movable swivel to go into the bung of the cask, or to lie flat as required. The oil is pumped from the tanks 5 and 6, through the pump 9, up tube 10, into the purifier 11 (in case of palm oil only), where it is decolorised by a stream of air being pumped through it. Where this is unnecessary, the oil is pumped directly into the soap kettle 12. This is fitted with a swivel-jointed skimmer 13, for running off the soap into the wooden troughs 14, 14, 14, where it can be made to flow into the soap frames 15, 15, 15, by raising the outlet slides indicated in diagram. In modern factories, however, the liquid soap is run direct to the cooling machine autoclave 16, or, if required for making special soaps, into the crutchers 17.

The soap kettle 12 is fitted with open and closed steam coils 18 and 19. Below the soap kettle 12 are placed the spent lye tank 21 and the semi-spent lye tank 20. Above the soap kettle is the lye tank 22 and the caustic soda tank 23, for supplying lye or caustic soda to the contents of the kettle. Water taps are also laid on for supplying water to the kettle. The semi-spent lye in tank 20, which is obtained from the soap, is used over again, but the spent lye in tank 21 is run down to the glycerine treating tank 22, which is fitted with a steam coil (closed) and an air mixing coil. The glycerine is here treated in the usual way with alum, hydrochloric acid, and caustic soda as described under glycerine. The glycerine is then pumped through the filter press 24 into the settling tank 25. It is here settled and filtered once more into the tank 26, whence it goes to the vacuum concentrators 27 and 29, and salt recovery box 28. The salt is taken out of the box 28, and is used again in salting out the soap, and the concentrated crude glycerine is run off and worked up for pure dynamite glycerine, as described later. Tank 30 shows the resin soap kettle. The resin and soda ash are placed in the iron tank 30, fitted with open and closed steam coils, and is there boiled up to make the resin soap, which is pumped up through pump 33, along the pipe 34, into the soap kettle 12; 35 is the causticising tank. The calcium carbonate sludge is run out either into an iron tank car, or is deposited in a sludge tank. The caustic soda (6-7 per cent. NaOH) is pumped into the storage tank 36, and is then pumped to the vacuum concentrator 38, where it is concentrated to 20-22 per cent. NaOH, and is then pumped back to the storage tank 37. It is pumped up as required into the caustic soda tank 23, and is run into the soap kettle from 23. The washings from the causticising tank 35 are pumped up to 39, and are used instead of water or lye in the soap kettle; for this purpose it is pumped back through 22. Sometimes the washings are used instead of water in the causticising tank 35.





OH  
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Na OH  
Settling  
Tanks.  
E'





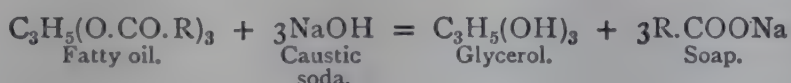
## Soap-making Processes where the Glycerol is set free but not separated from the Soap

These processes suffer from the economic disadvantage that the glycerol—a valuable product—is retained by the soap, and so is lost. They may be divided into three classes: (a) **Cold Process Soaps**; (b) **Hydrated Soaps** (which include “marine”) and “**Soft**” Soaps; (c) **High Pressure Soaps**.

(a) **Cold Process Soaps**.—Certain fats, principally those of the cocoa-nut oil and castor oil group, have the valuable property of being directly converted into soap at ordinary temperatures when mixed with concentrated caustic soda (sp. gr. 1.33, or 66° Twaddel, containing 24 per cent. NaOH), thus forming “Cold Process” soap.

The fat is weighed into an iron vessel provided with stirring apparatus, and is brought to the proper temperature (65° C. in cold weather, 50° C. in hot), and then the calculated amount of concentrated caustic soda or potash (or a mixture of both) is rapidly run into the vessel, and the whole thoroughly stirred until the soap begins to thicken.

If fillers are to be used, the intended amount of scent, sodium silicate, and sodium or potassium carbonate solution (“soda-ash lye” or “pearl ash”) is now stirred in; the mixture becomes thinner, and after a few minutes becomes thick. The paste is then run out into a wooden frame, and well covered up to keep in the heat. Combination proceeds in the frame, considerable warmth is evolved, and the mixture swells up, soap being gradually produced according to the equation:—



R represents the radicle of the fatty acid.

With small batches the process may be complete in two days. Usually, however, a week or more is allowed to elapse.

The great disadvantages of the “Cold Process” method are:—

1. Complete combination of fat and alkali are seldom secured; such soaps usually contain free alkali and unchanged fat.

2. The glycerol—a valuable commercial product—is retained in the soap and so is lost.

The advantages are: great simplicity in plant and operation; great rapidity of production.

The amount of soap—principally cheap scented toilet soap—made by this process is small. Some transparent soaps are also made this way.

(b) **Hydrated Soaps, Soft Soaps**.—**Soft Soaps** (see p. 117) are prepared by boiling together caustic potash and suitable oils at ordinary pressures until a sample when cold sets to a clear translucent mass. The mass is then boiled down until sufficiently concentrated and is put up in barrels, canisters, or drums for sale. They form soft, jelly-like masses. **Hydrated** soaps are manufactured in the same way as soft soap, but caustic soda is used instead of potash, and the fatty materials so chosen as to yield hard opaque products. **Marine soaps** (which see) are made this way from cocoa-nut oils (p. 116).

In order to produce a practically neutral soap, the quantity of caustic soda required for saponification must be carefully calculated from the saponification value of the fatty material employed. If proper quantities are taken it is quite possible to produce a practically neutral soap by careful working.

It is remarkable that other oils and fats, e.g., tallow, which alone cannot be saponified in the cold by concentrated caustic soda solution, are readily saponified when incorporated with oils of the cocoa-nut oil group, the heat which is evolved on the saponification of these latter oils apparently aiding the conversion of the former into soap. The process is essentially a rapid one. Lamborn states that for a 1,000-lb. frame the caustic soda must be run into the fat in one and a half to two minutes, the silicate in the same time, and the stirring (“crutching”) must be rapid and thorough for twelve to sixteen minutes. It is sometimes done by hand.



Every manufacturer employs his own formula. Two typical ones for hard crutched cold process soap are:—

## No. 1.

75 lbs. tallow.  
25 lbs. cocoa-nut oil (Ceylon).  
75 lbs. caustic soda lye, 35.5° Be., made from 74 per cent. caustic soda.  
125 lbs. "N" silicate of soda.  
20 lbs. potassium carbonate solution, 36° Be.  
Yield—320 lbs. soap.

## No. 2.

75 lbs. tallow.  
25 lbs. cocoa-nut oil.  
70 lbs. caustic soda lye, 35.5° Be., made from 74 per cent. caustic soda.  
100 lbs. "N" sodium silicate.  
17 lbs. potassium carbonate lye, 36° Be.  
Yield—288 lbs. soap.

When cold and hard the soap is taken out of the frame and cut into bars and pressed into tablets in the usual way (see pp. 104, 105).

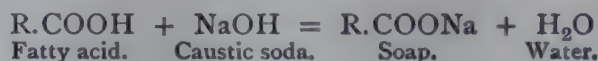
(c) **Hydrated Soaps prepared under Pressure.**—Here the fatty matters and caustic soda are simply heated together under high-pressure steam in autoclaves, the object being to cause the reaction to occur at a more elevated temperature and pressure in order to shorten the time of reaction and to simplify the procedure. In some processes the caustic soda and fat are pumped continuously into the boiler, and the finished soap pumped out simultaneously through a weighted exit valve, the process being a continuous one. **Bennet & Gibbs** use **sodium carbonate** solution, which, at a steam pressure of 15-20 atmospheres, corresponding to 190°-215° C. in the autoclave, readily saponifies the fat.

### Soap Making by Direct Neutralisation of Fatty Acids with Alkalis

These processes are growing in importance.

Since soaps are simply salts of fatty acids, obviously the most direct and simplest way to produce them is to directly neutralise the free fatty acids with caustic alkali or alkaline carbonates.

If **caustic soda** is used the process is very simple. The caustic soda is placed in a mixing machine ("crutcher"), the stirring apparatus set into rapid motion, and the fatty acids added in a rapid stream so that the entire charge is added in two to three minutes. Combination takes place thus:—

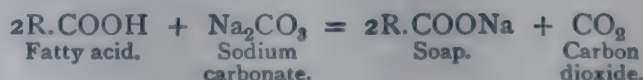


R represents the radicle of the fatty acid.

After five to ten minutes the mixture thickens, and "filling" (such as sodium silicate or sodium carbonate) is added. The temperature must not exceed 60° C. The mixing ("crutching") should proceed rapidly for fifteen to thirty minutes, the temperature being maintained between 60° C. and 70° C. by means of steam in the jacket with which the mixing machine is provided. The soap is then run into frames and allowed to cool.

A slight excess of alkali is necessary for complete combination. For certain textile soaps this does not matter. If a grained neutral soap is required the soap may be salted out with brine, and "fitted" as described on p. 103. In practice the fatty acid is always run into the alkali, and not *vice versa*, otherwise lumps are formed and the reaction does not proceed so smoothly.

If **sodium carbonate** is used instead of caustic the process becomes more troublesome; CO<sub>2</sub> is evolved thus:—



The CO<sub>2</sub> liberated is a source of trouble, since it causes the liquid to froth up, and consequently the mixing pan must be fitted with a large movable "curb"—a barrel or funnel-shaped top—in order to retain the froth, and the heating must be carried out slowly to prevent frothing over. The solution must be boiled until all the



sodium carbonate has been neutralised and the  $\text{CO}_2$  gas expelled. Then caustic soda is added and the soap boiled until it no longer absorbs more. Finally the soap is grained out with salt in the ordinary way.

Sodium carbonate is cheaper than caustic soda, nevertheless most manufacturers prefer caustic soda—especially as it is now manufactured so cheaply by electrolytic and other processes—since they consider that the slight saving in cost by using sodium carbonate is more than outweighed by the increased trouble and expense of working.

The fatty acids employed until recently were almost entirely confined to the “red oils” of the candle-maker (*i.e.*, oleic acid), and the resulting soaps were used for textile purposes and as the basis of certain soap powders. Within recent years, however, fatty acids have been obtained by first decomposing the fats and oils constituting ordinary soap stock by “*Twitchell's*” or some similar process (see p. 92), and the glycerol recovered; then the fatty acids so obtained are converted into soap by direct neutralisation as above described.

The great advantages of this latter method (which will in the near future probably entirely displace the older processes of soap-making) are (1) the glycerol is recovered from the fats *before making them into soap*, being immediately obtained in a concentrated and fairly pure form, which permits of its being worked up into the pure product far more easily and economically than when obtained from the impure soap lye of the ordinary method of making soap by boiling fats with alkalies. (2) The resulting operations of combining the fatty acids with caustic soda are rapidly and easily performed.

**Fatty Acids** are especially well adapted for making soft soaps with potash, for the glycerol in the original fat is recovered before treating the fatty acid with potash (see *Twitchell's Process*). In the ordinary way of making soft potash soaps by treating a neutral fat with potash and boiling down, all the glycerol is retained in the soap and so is completely lost.

**Other Methods of Soap-Making.**—Many attempts have been made to saponify fats or oils with lime, thereby producing an insoluble Ca soap + glycerol water, filtering off the glycerol water and working it up for pure glycerol; then converting the insoluble Ca soap remaining into ordinary soap by treating with  $\text{Na}_2\text{CO}_3$ :— $\text{Ca soap} + \text{Na}_2\text{CO}_3 = \text{soda soap} + \text{CaCO}_3$ , and filtering off the precipitated  $\text{CaCO}_3$ . This is *Kreibitz's Process*. See *Kreibitz*, English Patents, 4,092, 1905; 4,092A, 1905. **Barbé and Garelli** (English Patent, 12,210, 1907) heat fats with ammonia under pressure, thereby producing ammonium soaps and glycerol. The ammonia soaps are now decomposed by steam, the ammonia being boiled off, condensed, and used again. The free fatty acids float on the surface of the glycerol water and are separated by decantation and converted into soap by direct treatment with  $\text{NaOH}$ ; or the ammonia soaps are directly decomposed by a sodium salt:— $2\text{NH}_4 \text{ soap} + \text{Na}_2\text{SO}_4 = \text{sodium soap} + (\text{NH}_4)_2\text{SO}_4$  (see pp. 93, 99).

### Characteristics of Soap made from Different Classes of Soap Stock

Soap stock may be divided into the following classes, all of which exhibit well-defined chemical and physical differences:—

CLASSIFICATION OF SOAP STOCK

1	2	3	4	5
Cocoa-nut oil. Palm-kernel oil. ... .. ... ...	Olive oil. Olive oil foots. Cotton-seed oil. Pea-nut oil. Sun-flower oil. Corn oil.	Tallow. Greases. Palm oil. ... ... ... ...	Castor oil. Linseed oil. ... ... ... ...	Red oil. Rosin. ... ... ... ...

**Class 1. Cocoa-nut and Palm-kernel Oils.**—These oils saponify with great rapidity at ordinary temperatures with cold concentrated caustic soda or potash, with the evolution of much heat. This property peculiarly adapts them for soap manufacture by the cold process. Weak caustic soda solution,  $12^\circ$  Be.,



such as is used in the saponification of tallow, scarcely affects these oils in the cold, while lye of 20° Be. at least is required for making them into soap by the boiling process. These oils are characterised by the large amounts of glycerides of low molecular weight they contain; consequently they absorb more alkali and liberate more glycerol (12 per cent.) and give a firmer and higher yield of soap than any other oils used in soap-making. The addition of cocoa-nut oil to tallow and cotton-seed oil in manufacturing settled ("grained") soap, yields a soap much superior to that produced from either stock alone.

Cocoa-nut oil soap is white, hard, and brittle, and gives a quick, profuse, but thin lather with both salt and fresh water. The soap is capable of absorbing enormous amounts of water and mineral matter ("filling," such as sodium carbonate and sodium silicate), yielding a firm soap. It requires a very large amount of salt to throw it out of solution, being very soluble both in fresh and salt water, and thus is a "marine" soap. A 50 per cent. cocoa-nut oil soap requires 15-20 per cent. of salt in the stock lye to throw it out of solution, against 7-10 per cent. required for ordinary tallow stock. The graining of pure cocoa-nut oil soap with salt is very unsatisfactory. Such soaps, unless very carefully saponified, become rancid with age.

**Class 2. Olive, Cotton-seed, and Corn Oils.**—All these oils consist principally of olein—the glyceride of oleic acid.

**Olive oil** saponifies readily with lyes of very different densities, yielding a greenish-coloured soap, called "Castile," which gives a thin, slimy but abundant lather peculiar to all soaps containing much oleate. The soap is an ideal one for toilet or textile purposes, but is very expensive. **Refined cotton-seed oil** saponifies with difficulty, yielding a soap which, unless very carefully saponified, suffers a very rapid deterioration, becoming discoloured and rancid on keeping. Containing much olein, the oil yields a thin soap lacking the body of tallow soap; by mixing with large proportions of soda-ash and sodium silicate, a firm soap is produced, which is much used in the United States as a laundry soap.

All soaps consisting principally of sodium oleate (for example, olive-oil and cotton-oil soaps) are much more soluble in water than soaps made from tallow, and therefore containing much sodium stearate. Moreover, such oleate soaps readily absorb moisture from the air, and thus give rise to "sweating." The yield of glycerol is about 10 per cent.

**Class 3. Tallow, Palm Oil, Greases.**—The principal glycerides present are stearin and palmitin. Tallow is readily saponified with weak lye, between 10°-15° Be., and yields a firm soap of good body, and easily grained by 7-10 per cent. of salt in the lye. The soap is one of the least soluble, and it yields an inferior but persistent lather, excellent for shaving purposes, but overlooked by the public, who demand a freely lathering soap. On ageing, tallow soap becomes so hard that it may injure fabrics. It is best mixed with other stock, imparting body and firmness to the resulting soaps. **Palm oil** contains much palmitin, and in general properties produces a soap much like tallow soap. It yields a slow but thick and lasting lather. Is a good textile soap. These oils yield about 9 per cent. of glycerol.

**Class 4. Linseed and Castor Oils** are very readily saponified, yielding a quick-lathering, very soluble soap, of pale brown colour and characteristic odour. The oils are used for making transparent soaps and for the green *Sapo verdigris* of pharmacy.

**Class 5. Red Oil and Rosin.**—Red oil is commercial oleic acid, and consequently directly combines with caustic soda or sodium carbonate to produce the soap sodium oleate. Red oil, or olein soap, is much used in the textile industry, being similar to the soaps discussed under Class 2 (which see). **Rosin** is also an acid body, and consequently directly combines either with caustic soda or sodium carbonate to produce a soap which, although possessing valuable detergent properties, is very hygroscopic, very soluble in water, and soft. The presence of rosin in other soaps is betrayed by a stickiness and a readiness to "sweat." Rosin soaps added to tallow soaps modify their hardness and improve their properties for many purposes. Rosin must not be used as a constituent of textile soaps (which see, p. 114).



## Various Kinds of Soaps

**Milled Soap, Toilet Soap.**—The best toilet soaps are manufactured by the process of milling, whereby they acquire a finish and quality otherwise unattainable. Soaps thus manufactured are certainly the most economical, since they contain no moisture and consequently do not shrink or lose weight (as do all toilet soaps not milled). Moreover, they improve on keeping—other soaps usually deteriorating. The soap must be a grained, settled soap, of good quality, and perfectly neutral (0.3 per cent.  $\text{Na}_2\text{CO}_3$  and 0.5 per cent.  $\text{NaOH}$  are the utmost limits allowable). The racked and fairly dry bars of soap are cut into shavings by a rotatory cutting machine ("soap-chipper") and these are dried by steam in a drying-room until the water is reduced from 30 per cent. (the usual amount in freshly made soap) to anything between 14 per cent. and 3 per cent.

The dried shavings are then mixed with the necessary colouring matters and perfumes in a zinc-lined box, and then are ground in a **Toilet Soap Mill**, which consists of polished stone rollers of the best Quincey granite, arranged horizontally or with a pitch as shown.

The soap as it comes from the last roll is detached by a knife, and comes out as translucent homogeneous ribbons of the thickness of paper. Three or four millings are enough for a cheap soap, and seven or eight for better quality soaps. From the mill the mass of soap ribbons is fed into the "plodder," where, by means of a spiral screw, the mass is forced under great pressure through a number of holes in a plate, so that the soap passes this part of the machine in the form of a number of thick threads, which are again squeezed

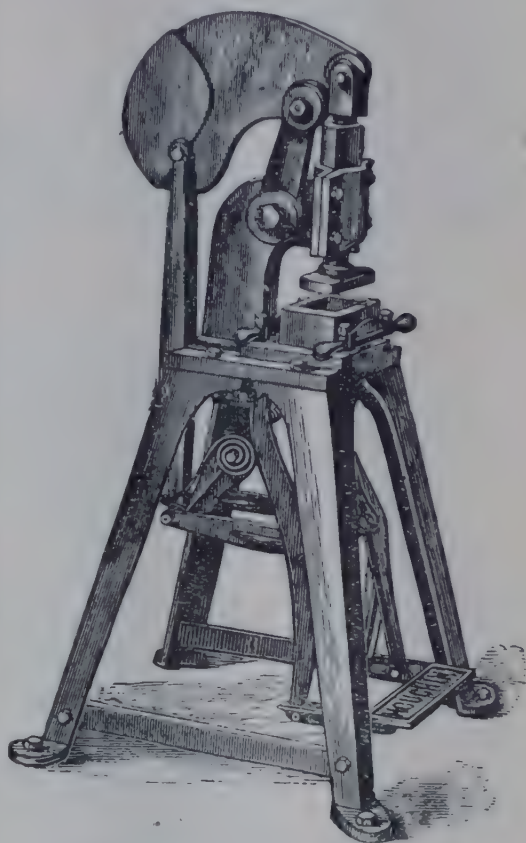


FIG. 35.—Hand Soap Press.  
(Houchin, New York.)

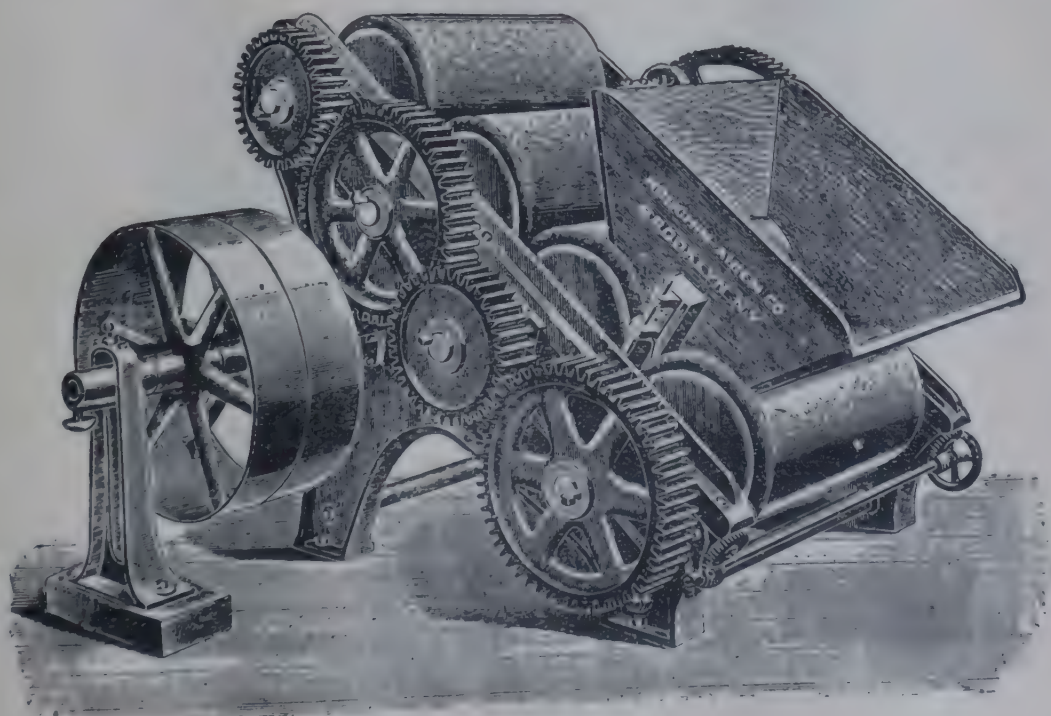


FIG. 36.—Toilet Soap Mill.



together and coalesce to come out of the plodder mouth in the form of a continuous bar. Sometimes it is necessary to warm the mouthpiece of the plodder (which is provided with a water jacket and a small Bunsen burner) in order that the soap may be somewhat softened and thus pass through the perforations of the disc without being broken by successive revolutions of the screw.

The best plodders are porcelain lined.

The continuous bar of soap is cut automatically as it comes forth from the plodder into pieces, each weighing about 4 oz., which are then rapidly stamped in presses into the oval tablets in which toilet soap is sold.

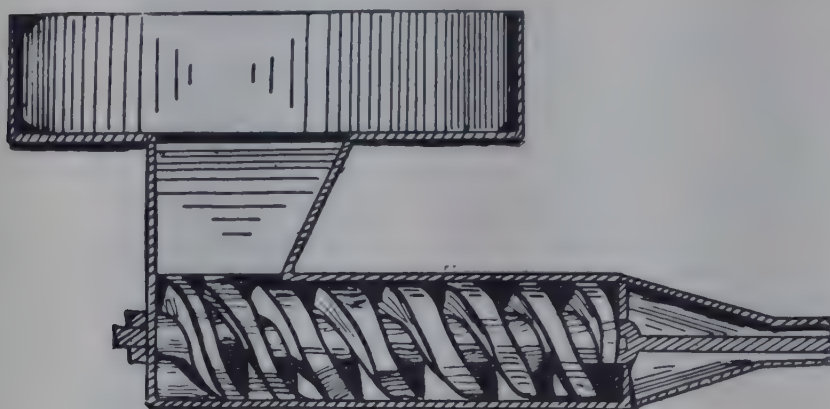


FIG. 37.—Section of Plodder.

drying and chipping are avoided. The fluid soap, just as it comes from the kettle or crutcher, (where it is perfumed and coloured) is poured down a hopper surrounding a series of water-cooled cylinders, from which the soap as it cools and solidifies is detached by knives in the form of thin shavings; then, falling upon a series of endless belts of wire cloth enclosed in a chamber through which dry hot air is continually driven, is rapidly dried, and dropping upon successive layers of underlying and moving belts, is finally discharged with its water reduced to 12 per cent. in a few minutes. The dried chips are then passed on to the mill and plodder in the usual way. This machine is also used on the large scale for the manufacture of "soap chips" and "soap powder" (see p. 115).

**Continuous Soap-Drying Apparatus.** — The process of toilet soap-making, as described above, requires at least seven days. The period may be reduced to only ten to fifteen minutes by employing the special machine illustrated in Fig. 39, whereby the lengthy processes of framing, slabbing, cutting,

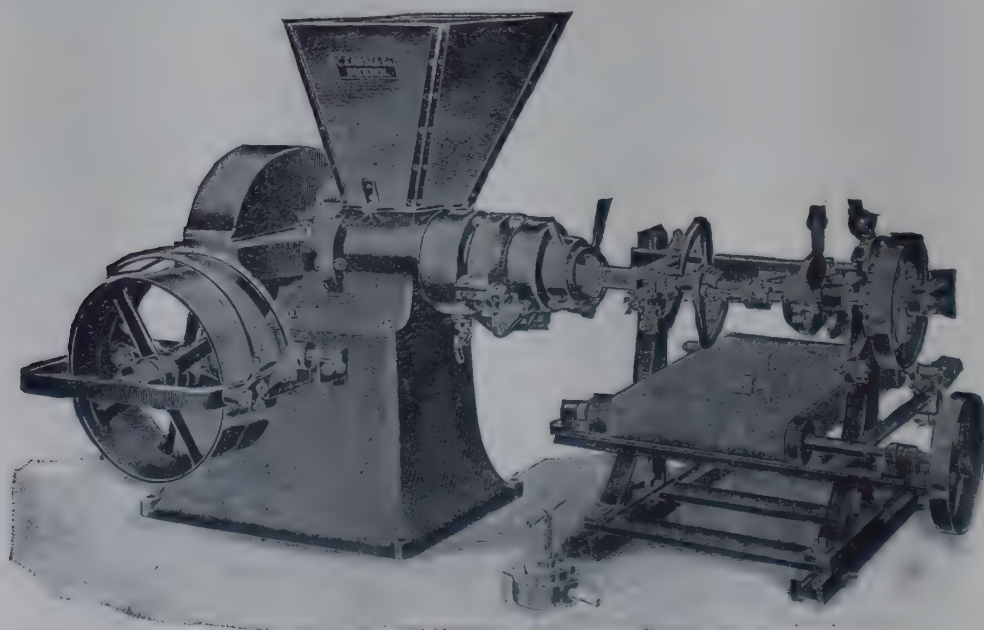


FIG. 38.—Plodder, showing automatic arrangement for cutting the bar of soap into small pieces for stamping. (Rost & Co., Dresden.)

**Transparent Soaps** may be made by mixing soap with (1) alcohol, (2) alcohol and glycerol, (3) alcohol and sugar, or (4) sugar alone.

**1. With Alcohol Alone.**—Shavings of a good quality soap, carefully dried in hot air, are gently warmed in a still with an equal weight of rectified spirit (heated on water bath) until the soap is dissolved. The excess of alcohol is distilled off and collected and used again. The clear liquid left behind is run into frames, cooled



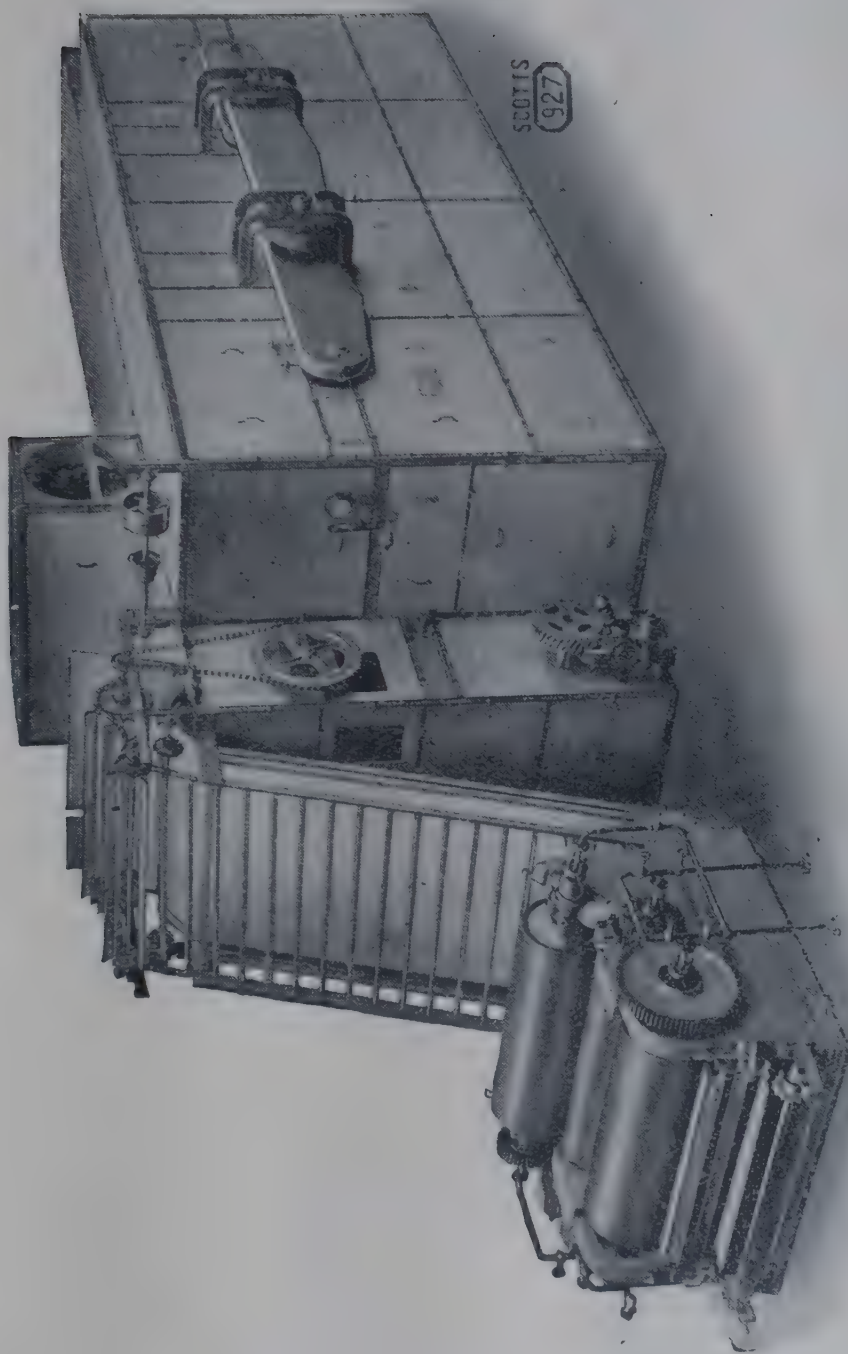


FIG. 39.

(Messrs George Scott & Son Ltd., London and Leven.)

*By courtesy]*

cut into pieces, pressed, and allowed to season in dry air. The best, but most expensive, soap is thus produced.

**2. With Alcohol and Glycerol, or Sugar.**—These and the succeeding classes of soaps are best made by the “cold process,” from about equal parts of cocoa-nut oil and tallow, together with a quantity of castor oil; the latter oil greatly conduces to the transparency and at the same time diminishes the quantity of alcohol, glycerol, or sugar needed for transparency.

The melted **fats** are placed in a steam-jacketed crutcher, heated to  $50^{\circ}\text{C}$ ., and the proper amount of lye at  $38^{\circ}\text{Be}$ . mixed in. On standing for over three hours the temperature rises spontaneously to over  $80^{\circ}\text{C}$ . Any glycerol is mixed in before adding the lye. Alcohol should be mixed in after the addition of lye and before allowing the mixture to stand. After the period of standing is over, sugar and soda-ash solutions at  $80^{\circ}\text{C}$ . are run in and vigorously mixed. After this, the mass is allowed to stand while samples are taken. Finally the soap is run out into frames, being strained as it does so. When cold and solid it is cut and pressed.

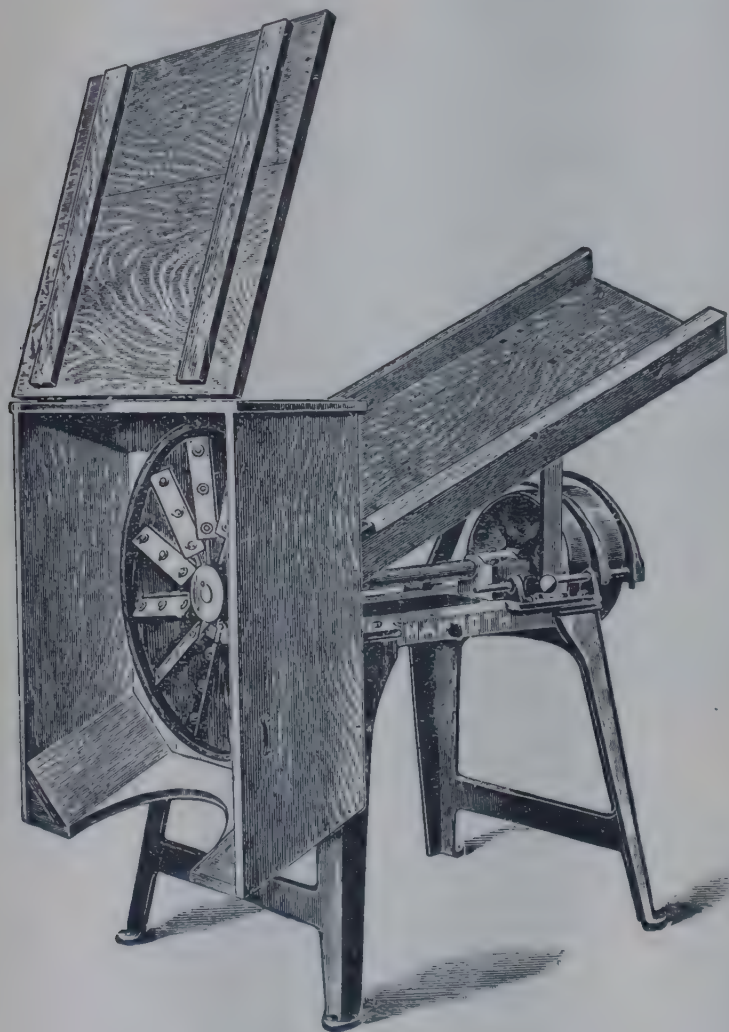


FIG. 40.—Soap Chipper.

The following is a typical formula for an alcohol-glycerol transparent soap: Cocoa-nut oil, 100-120 lbs.; edible tallow, 100-60 lbs.; caustic soda lye of  $38^{\circ}\text{Be}$ ., 100-90 lbs.; alcohol (95 per cent.), 80-60 lbs.; glycerol, 40-60 lbs. This also is an expensive soap, but a cheaper transparent soap containing **alcohol and sugar** may be made from the following ingredients: Edible tallow, 100 lbs.; cocoa-nut oil, 100 lbs.; castor oil, 30 lbs.; alcohol (95 per cent.), 100 lbs.; sugar, 25-60 lbs.; water, 40-65 lbs. In cheaper soaps a quantity of soda-ash solution is added.

A still cheaper transparent soap, **without alcohol**, but containing **sugar** and castor oil, is as follows: Cocoa-nut oil, 100 lbs.; edible tallow, 80 lbs.; castor oil, 103 lbs.; sugar, 80 lbs.; caustic soda lye of  $38^{\circ}\text{Be}$ ., 146 lbs.; soda-ash solution of  $36^{\circ}\text{Be}$ ., 40 lbs.; water, 85 lbs. In the absence of alcohol and glycerol, the proportions of sugar and castor oil are increased in order to attain transparency.

### Textile Soaps

**A Soap for Scouring Raw Wool** must dissolve freely at  $50^{\circ}\text{--}55^{\circ}\text{C}$ ., be quite neutral (free alkali deteriorates wool), free from uncombined fat, without rosin, sodium silicate, mineral oil, or other filling material. It should not contain more than 30 per cent. water, must be free from nitrobenzene or other perfuming stuff; it must not have an unpleasant smell when rubbed in the palm of the hand. A neutral soda soap, made from red oil (oleic acid) and sodium carbonate, is much used. A neutral olive-oil potash soap is best, but too expensive except for the very best quality goods. Cocoa-nut and cotton-seed soaps are useless unless they are quite free from odour, which otherwise persists in the finished goods. Cotton-seed and corn-oil soaps (made from semi-drying stock) are difficult to remove,



impart cloudiness to the milled wool, as well as causing odour and stickiness. Palm-oil soap is superior to pure tallow soap, the latter being somewhat insoluble.

**A Silk Textile Soap** must contain no free caustic soda or potash, but may possess a very slight degree of alkalinity due to a trace of sodium or potassium carbonate. A neutral potash soap from olive or lard oil is often used, as well as the cheaper soda olive-oil soap, and hard or soft palm-oil soap. Tallow soaps are unsuitable, as also are cotton-seed oil soaps. Soaps made from red oil (oleic acid) are suitable.

**A Cotton Textile Soap**, for which there is little demand, may contain dilute alkalis, since cotton is not injured by dilute caustic soda.

**A Soap for Printers' Use** must be fairly soluble in water, and so palm, olive, and cocoa-nut oil soaps are used instead of tallow soap. Such soap must be quite neutral, since free alkali may alter the colours or cause them to "bleed." Rosin, cotton-seed oil, and linseed-oil soaps cause colours to bleed, and so are unsuitable. Also the soaps must not impart any odour to the cloth.

**A Soap for the Woollen Dyer** may be made from tallow, palm, or olive oil, and be of a very slight degree of alkalinity. Before woollen cloths or yarns are dyed any oil they contain must be removed by soaking them in a very common soap, usually made from bone fat and cotton-seed oil, and slightly alkaline in reaction.

**Soap Powders, Dry Soaps, Washing Powders.**—Soap powder supplies the demand for a cheap quick detergent for cleansing coarse articles. It is a mixture of soap (usually made from low-grade grease) and soda-ash. The soda-ash takes up water of crystallisation, and this dries the soap. Without the addition of the soda-ash it is difficult to produce a true soap powder from pure soap. Rosin cannot be used, because, owing to the deliquescence of rosin soap, the soap powder becomes lumpy. The soap, grained, separated from the waste lye, closed, and finished very thin, is run directly from the kettle into the mixing machine (crutcher), and then the sodium carbonate (soda-ash) added in successive amounts until the proper quantity is present, and finally the sodium silicate is usually added. The usual proportions are: 600 lbs. soap, 600 lbs. soda-ash, 100 lbs. sodium silicate. After mixing thoroughly, the mass is run into frames in the usual way; in some establishments it is poured in a layer over the floor, and the mass, when cold and firm, is broken into lumps, which are then smashed into small pieces in a disintegrator, and finally the fragments are ground to a fine powder in a special mill, and the powder stored either in casks or in cardboard cartoons. Sometimes sand, sodium sulphate, fullers' earth, talc, etc., are added to soaps of this nature.

A rapid method of manufacture, now adopted in most large establishments, is to pour the fluid soap direct from the crutcher into the hopper of the continuous soap-drying machine described on p. 112, whereby the soap is discharged, dried and disintegrated, ready for grinding, in ten to fifteen minutes from the time of entering the machine. Thus the tedious processes of framing, cooling, slabbing, etc., which occupy several days, are entirely avoided.

**Peroxide Soaps.**—Many efforts have been made to manufacture soaps containing active oxygen, as such soaps have valuable disinfecting and bleaching properties. Thus Henderson (English Patent, 14,784, 1906) treats cocoa-nut oil, prior to the manufacture of soap, with ozonised air, and the soap made with the product has an oxidising and antiseptic action, and is free from a cocoa-nut smell.

Wolffenstein (English Patent, 16,823, 1908) produces **non-alkaline** soap preparations containing oxygen as peroxide by causing free fatty acids to act at 100° C. upon alkali salts of peracids, such as sodium percarbonate, perborate, persulphate, etc. It is very remarkable that the salts of the peracids are stable enough to be used thus. The soaps have bleaching and disinfecting properties.



Byx (English Patent, 7495, 1909) dehydrates sodium perborate, and mixes it with fatty acids. The product is said to be stable. See also English Patents, 15,900, 1907; 7,619, 1909.

These methods promise to become industrially important.

**Scouring Soap Base** is best made from cocoa-nut oil. The glycerol, amounting to over 12 per cent., should be separated. Cocoa-nut oil requires for saponification by the boiled process caustic lye of at least 20° Be. The oil is first added to the kettle, then much lye at 20° Be. is run in. Saponification rapidly ensues. If too little lye is present the mass tends to thicken in the kettle; in this case more steam is admitted and lye rapidly added. Towards the end of the operation lye at 25° Be. is added. Cocoa-nut oil soap requires more salt to grain than ordinary soap, and may on the first boiling be grained with strong lye up to 35° Be., and the lye (strongly alkaline) separated may be used for saponifying a fresh quantity of oil. The second graining is with salt. Then the soap is closed with water, grained with 20° Be. lye, boiled as on the strengthening charge, the lye withdrawn, and the soap finished by adding water, when it is ready to be used for mixing.

**Castile Soap** is made by settling a pure olive-oil soda soap. Owing to the high price of olive oil it is usually, in part, replaced by pea-nut, cotton-seed, or light-coloured red oil. A good imitation Castile soap consists of 65 per cent. olive oil and 35 per cent. tallow. The green colour is sometimes enhanced by adding chlorophyll compound.

**Marine or Salt-water Soap** is made from cocoa-nut oil, as described under "scouring soap" base. The cocoa-nut oil soap is a very firm one, which is easily soluble both in fresh and salt water, and yields a profuse lather. The soap must be free from filling of any kind, entirely soluble in salt water, *must not contain more than* 3 per cent. free sodium carbonate, 0.5 per cent. free caustic soda, 0.3 per cent. salt, 0.5 per cent. mineral matter (silicate of soda, sodium sulphate, etc.), 55 per cent. water.

**Protein Soaps.**—When protein matter—such as that contained in the germ of various cereals, oatmeal, rice gluten, etc.—is acted on by concentrated NaOH solution, the soap of amino-acids is produced which may be used as a substitute for marine soap, being said to leave no odour and to wash better in brine than marine soap. See English Patents, 17,999, 1905; 23,546, 1905; 5,620, 1909; 20,089, 1909.

**Mottled Soap** is made from ordinary settled soap of good quality by finishing thin, and adding insoluble colouring matter (venetian red, ultramarine blue, yellow ochre, copperas or ferrous sulphate) in the proportion 4-8 oz. to 100 lbs. of soap; the soap is well boiled up, and run into hot frames and crutched by hand until the temperature sinks to 60° C., when all danger of the mottling agent sinking to the bottom is passed. On slowly cooling, the soap crystallises out, and the pigment is expelled from the crystallising soap into portions which are still fluid, and this portion finally cooling, the foreign matter remains mixed with the softer or more fluid soap. To obtain a good mottle the soap must at first be very fluid, and must slowly cool in order that the crystallising should not be too rapid, otherwise only a discoloration or a very fine mottle results. Such mottled soap is usually made in small batches as it is difficult to incorporate the pigment evenly throughout a large mass of soap.

**Settled Rosined Soap** is made as described on p. 103, and is the one generally used for ordinary washing purposes, since the rosin imparts to the hard tallow soap softness and lathering power, besides being of considerable detergent value itself. For certain purposes, however, the presence of rosin in soap is very injurious.



**Pure Rosin Soap**, *i.e.*, sodium rosinate—prepared by dissolving colophony (ordinary rosin) in caustic soda—is used on a large scale for paper sizing (see Paper Making). It is described on p. 199 under **Paper Making**.

**Potassium Soaps, Soft Soaps**.—Soft soap is sometimes defined as soap made from low-melting point stock by use of caustic potash. Such soap is semi-transparent, soft, unctuous, and very soluble in water and deliquescent. It must be noted, however, that while *all* potassium soaps are soft, some sodium salts now manufactured are also quite soft (see p. 107).

Linseed oil, cotton-seed oil, corn oil, olive oil, olive-oil foots mixed with tallow, and tallow, are the stocks usually used.

A potash linseed-oil soap retains its transparency throughout summer and winter. Rosin may be used in very small proportions to increase its lathering and detergent qualities. Red oil forms a good, odourless potash soap; tallow produces a white potash soap.

The saponification is completed in the usual way, but without graining, and the soap is run through the crutcher directly into barrels and stored in a cool place. The glycerol is thus usually retained in the soap. Usually 100 lbs. of stock yield 225-250 lbs. of potash soap. About 30 lbs. of potassium chloride can be incorporated, giving a yield of 270-280 lbs. Higher yields than this are obtained by adding a binding agent, such as starch. Fillings of chlorides, carbonates, and silicates of potassium and sodium are used, the sodium salts, however, being less preferable. Soap powder has displaced these soaps.

**Floating Soap** is made by churning up a pure white settled and perfectly neutral soap (best made from tallow mixed with 25 per cent. cocoa-nut oil) in a special crutcher, the whole being heated about 80° C. The soap is beaten up into a froth and air incorporated with it to such an extent that the mass is lighter than water.

**Shaving Soap** is made from the best edible tallow by the grained process; it must be perfectly neutral. Cotton-seed and cocoa-nut oils are unsuitable as stock ingredients. The lye used for saponification usually consists of 25 per cent. KOH and 75 per cent. NaOH. The soap should contain very little water, and must be milled. During milling 8-10 per cent. of glycerol and 1 per cent. of tragacanth gum (which gives a permanent lather) are introduced.

**Medicated Soap** consists of ordinary soap mixed with small quantities of disinfecting or germicidal agents, such as phenol, cresol, etc. Almost invariably they are quite useless for the purpose for which they are intended, being scarcely more effective than a pure neutral soap, which itself has a considerable germicidal action, and is a valuable, although slow, disinfectant.

**Formaline Soaps**.—**Liquid** formaline soap consists of 10-25 per cent. formaline added to olive oil, alcohol, and essential oils. **Solid** formaline soap consists of 5 per cent. paraformaldehyde added to soap. Strong disinfectant.

**Iso Soap** is a solid sulphonic derivative of castor oil. Gives clear neutral solution, and forms, even with the hardest water, no insoluble lime salts. Hence is used for washing, dressing, bleaching, etc., in textile trades.

### Filling Agents

A very great number of substances are incorporated into soap.

**Rosin** is a proper constituent of soap, the sodium salts of the rosin acids possessing valuable detergent properties.

**Sodium Silicate and Borate** also possess detergent properties, but are often used in such large quantities in the cheaper soaps as to almost be regarded as adulterants. Silicated soaps harden on ageing, the silicates imparting firmness to a soft inferior soap. Ultimately such soaps become stonelike as regards hardness.

## ANALYSIS OF SOAP

The following is Dr Leed's scheme (*Chem. News*, xlviii. 67) for the complete analysis of soap:—

Weigh out 10 g. of sample. Dry at 110° C. Loss=water. Extract with petroleum ether.		Residue is soap and mineral constituents. Treat with alcohol.	
<i>Extract</i> is uncombined fat. Dry at 110° C., and weigh.	<i>Extract</i> is soap, glycerol, and free alkali. Add 2-3 drops of $\frac{N}{10}$ $H_2SO_4$ phenolphthalein, titrate with $\frac{N}{10}$ $H_2SO_4$	<i>Residue.</i> — $Na_2CO_3$ , $NaCl$ , $Na_2SO_4$ , sodium silicate, starch, and insoluble residue. Wash with 100 c.c. water.	
	Add large excess of water, boil off alcohol, decompose with excess of $\frac{N}{1}$ $H_2SO_4$ , boil, filter, wash.	<i>Filtrate.</i> — $Na_2CO_3$ , $NaCl$ , $Na_2SO_4$ , sodium silicate. Divide into four equal parts.	
$\frac{N}{10}$ $H_2SO_4$ used is due to free caustic alkali. Calculate as $NaOH$ .	<i>Filtrate.</i> Combined soda and glycerol. Titrate excess of acid back with $\frac{N}{10}$ $NaOH$ .	$Na_2CO_3$ . Titrate with $\frac{N}{10}$ $H_2SO_4$ and calculate as $Na_2CO_3$ .	$Na_2SO_4$ . Precipitate with $BaCl_2$ , weigh the $BaSO_4$ , calculate as $Na_2SO_4$ .
	After titration evaporate dry on water bath. Extract with absolute alcohol, evaporate the filtered solution in a weighed flask. Weigh any glycerol.	Residue, fatty acids and rosin. Dry at 110° C. <i>Estimate the rosin.</i> Subtract this. Difference = fatty acids.	<i>Sodium Silicate.</i> Decompose with $HCl$ , and determine soda combined in silicate and silica.
<b>Express Results thus—</b>			
Per cent.	Per cent.	Per cent.	Per cent.
Fatty acids - . . . . .	Sodium carbonate . . . . .	Silica - . . . . .	Soda in sodium silicate - . . . . . Lime - . . . . .
Rosin - . . . . .	" hydrate - . . . . .	Soda in sodium silicate - . . . . .	
Soda (existing as soap) - . . . . .	" chloride - . . . . .	Lime - . . . . .	
Water - . . . . .	" sulphide - . . . . .		

*Residue.*—Starch and insoluble residue. Dry, filter, and weigh; the starch and insoluble residue starch. Convert into  $C_6H_{12}O_6$ , titrate with Fehling's solution, subtract the weight of starch found. The difference is the insoluble mineral constituents.



**Petroleum Naphtha**, to the extent of 10 per cent., is sometimes incorporated in soap in order to increase its detergent action. The petroleum is mixed with a rosin soap mass, and the mixture added to the common soap.

**Colouring Matters** and perfumes (ethereal oils) are added, either to disguise inferior and evil-smelling and discoloured soap, or to please intending buyers.

**Scouring Soaps** often contain sand, kieselguhr, powdered pumice, etc. Some soaps contain sulphur, flour, talc, china clay, salt, etc. etc.

**Persulphates, Percarbonates, and Perborates** have been added to soaps in order to give them bleaching and disinfecting properties (see Peroxide Soaps, p. 115).

**Statistics.**—The following numbers show the amount of soap exported by the United Kingdom in 1910:—

	Cwt.	Value.
Soft soap - - - - -	32,116	£24,487
Household and laundry soap in bars or tablets	1,345,598	1,357,776
Polishing and scouring soap - - - - -	9,867	16,070
Soap powder - - - - -	26,478	30,790
Toilet soap - - - - -	74,145	357,781
Other sorts (including cotton-seed oil soap) -	4,259	10,639
<b>Total of soap - - -</b>	<b>1,492,463</b>	<b>£1,797,543</b>

The value of the imported soap in 1910 (principally household or laundry) was £454,000. The greater part of the soap produced in the United Kingdom is consumed at home.

The United States in 1910 imported 3,928,000 lbs. (value, 499,000 dols.) of toilet and fancy soap, and \$247,000 worth of other varieties. The export in the same year was:—*Toilet or fancy soap, value, \$1,480,000. Other kinds, 45,716,000 lbs. Value, \$2,141,000.*

## ANALYSIS OF SOAP

**Rosin.**—To detect rosin, dissolve some of the fatty acids above separated in warm acetic anhydride, cool, run in slowly sulphuric acid of sp. gr. 1.53 (made by mixing 34.7 c.c. concentrated  $H_2SO_4$  with 37.5 c.c. water, and cooling). A fugitive violet colour indicates rosin. Cholesterol gives same reaction, and should be removed in original soap before liberating the fatty acids by shaking out with ether.

To estimate rosin, weigh 2-3 g. of liberated and dried fatty acids into a flask, dissolve in ten times their volume absolute alcohol (not 90 per cent. alcohol), cool flask in cold water and drive for forty-five minutes a current of dry HCl gas through the liquid, stand for one hour, dilute with five times the volume of water, boil till clear, extract thoroughly in a separating funnel with ether, separate ethereal extract which contains the rosin, wash with water until all HCl is removed from it (test wash water with  $AgNO_3$ ), add 50 c.c. alcohol, and titrate with standard NaOH, using phenolphthalein as indicator. Each c.c. of  $\frac{N}{1}$  NaOH used up corresponds to 0.346 g. rosin.

**Glycerol.**—For detection and estimation, see Glycerol.

**Sugar** is sometimes present to 25 per cent. in cheap transparent soap. Estimate in usual way with Fehling's solution, diluting to avoid oxidation of glycerol. If much glycerol is present add slaked lime to combine with the sugar, add same amount of washed and recently ignited sand, boil down to a syrup, cool, pulverise, exhaust in a corked flask with 80-100 c.c. of alcohol-ether mixture (in equal volumes). The solution contains the glycerol (free from sugar), which is estimated by evaporating in usual way.

**Starch** is detected by a microscopical examination of residue insoluble in alcohol. Confirm by iodine test. For estimation see Starch.

**Dextrine** contained in the water solution with the sugar is estimated by precipitating with alcohol, stirring vigorously with a glass rod in a weighed beaker, pouring off the aqueous liquor, washing residue with alcohol, drying at 100° C., and weighing.

**Gelatine** is detected by washing the alcohol-ether insoluble residue with hot water, and testing filtrate with tannic acid.

TABLE OF ANALYSIS OF VARIOUS SOAPS (*Hope*)

Description of Soap.	Origin.	Fatty and Rosin Anhydrides.	Soda, Na <sub>2</sub> O, existing as Soap.	Silica.	Soda as Silicate.	Caustic and Carbonate of Soda.	Sodic Chloride.	Sodic Sulphate.	Lime, Oxide of Iron, etc.	Water.	Total.	Fatty and Rosin Acids.
White, No. 1	Tallow	69.06	8.98	0.01	<i>nil</i>	0.27	0.49	0.16	0.07	21.14	100.18	71.20
" 2	Tallow and cocoa-nut-oil	60.50	6.82	0.06	"	0.06	0.11	0.12	0.16	32.20	100.03	62.36
" 3	"	55.71	6.90	0.03	"	0.92	0.18	trace	0.08	36.54	100.36	57.44
" 4	"	44.27	6.23	7.02	2.36	0.75	0.32	0.34	0.34	38.14	99.77	45.64
Cold water, No. 1	Tallow, rosin, and cotton-seed oil	71.30	7.98	1.07	0.48	0.75	0.36	0.30	0.16	17.44	99.84	73.50
" 2	"	49.95	7.00	2.34	1.01	0.38	0.51	<i>nil</i>	0.50	38.18	99.82	51.50
Olive oil, No. 1	Olive oil	71.20	7.58	0.06	0.03	0.22	0.66	0.17	0.20	19.70	99.82	73.40
Marseilles, No. 1	Chiefly olive oil	62.66	7.27	0.06	0.03	0.77	0.76	0.30	0.16	28.20	100.21	64.60
Palm oil, No. 1	Palm oil	59.28	6.65	0.42	0.01	0.39	0.47	0.13	0.16	32.35	99.86	61.08
Mottled	Palm-nut oil	38.89	5.76	6.40	1.29	1.62	1.78	0.72	0.03	38.70	95.19	40.10
Satinet	Tallow and rosin	59.92	6.76	0.02	<i>nil</i>	0.92	0.41	0.37	0.05	31.30	99.75	61.77
Glasgow almond	"	42.41	4.14	5.64	1.59	2.76	0.37	trace	0.14	42.88	99.93	43.72
Pale rosin, No. 1	"	60.90	7.22	0.04	<i>nil</i>	0.10	0.46	0.12	0.02	31.22	100.08	62.78
" 2	"	48.20	5.00	0.42	0.18	0.15	0.65	0.10	0.10	45.00	99.80	49.65
" 3	"	39.92	4.70	0.62	0.25	0.20	1.48	0.18	0.15	52.40	99.90	41.15
Milling	...	63.06	7.25	0.02	<i>nil</i>	0.10	1.65	0.15	0.30	27.47	100.00	64.95
Yellow (for foreign markets)	...	10.90	1.36	0.03	"	trace	2.57	0.56	0.14	84.00	99.56	11.20
Marine (for emigrants)	Palm-nut oil	19.42	3.11	9.00	3.98	3.00	5.13	0.35	0.16	53.32	97.47	20.02



**Phenol or Cresol in soap** is roughly estimated by dissolving 100 g. of soap in hot water, making alkaline with NaOH, precipitating soap with salt, filtering off soap and washing it on filter with saturated brine, boiling down the brine solution, precipitating any dissolved soap again with brine, filtering, boiling filtrate to small bulk, transferring solution to a 50 c.c. stoppered graduated cylinder, adding salt so that some remains undissolved, acidifying with sulphuric acid, and reading off the volume of separated phenols, each c.c. representing 1 g. of phenol. For greater accuracy dissolve the phenols in ether, distil off ether, and estimate by *Koppeshaar's method*.

For further details the reader should consult one of the larger treatises on soap, or Allen's "Commercial Organic Analysis."

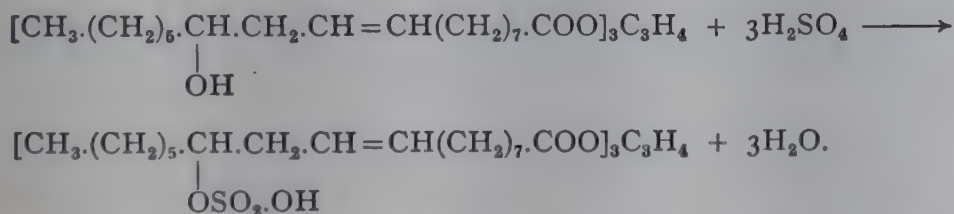
**Acknowledgments.**—The author has pleasure in thanking Mr W. H. Stephens, A.R.C.S., for expert advice regarding the newer processes employed in the soap industry.

**Soapless Detergents.**—Although sulpho-derivatives of fatty acid compounds have been used for about seventy years, their use as wetting out agents and detergents has only become widespread in recent years. The early use of sulphated castor oil was mainly confined to cotton dyeing and printing with the alizarin dyestuffs, such as Turkey-red. Sulphated castor oil has therefore been called Turkey-red oil. It acted similarly to a mordant when used in the form of mixture of its alkali salt and unsulphated castor oil. The cotton to be dyed was dipped in a 5 per cent. emulsion of Turkey-red oil in water and then into the dye-bath. The action of Turkey-red oil is now generally held to be that of a wetting and emulsifying agent in dyeing because it has been found to be equally effective with dyes which do not require a mordant.

More recently it has been discovered that for maximum wetting capacity and detergent properties a wetting agent should contain an alkyl chain at least twelve carbon atoms long, together with a highly polar terminal group.

First it is necessary to consider the original sulphated oils. In Turkey-red oil, the strongly polar sulpho group is attached at approximately the centre of a  $C_{18}$  carbon chain. The specific properties on account of which these products are useful are not so highly-developed as they are in those compounds where the sulpho-group is attached at the end of the carbon chain.

For the preparation of Turkey-red oil see p. 43. The reaction that takes place is



Then the free hydroxyl group of the sulphuric acid is replaced by sodium giving an emulsifiable product.

Modern wetting agents may be listed as six types, although new ones are always under investigation.

1. The Igepons—higher acyl derivatives of hydroxy or amino-alkyl sulphonic acids.
2. Salts of monosulphuric esters of higher fatty alcohols.
3. Alkyl derivatives of aromatic sulphonic acids.
4. Salts between triethanolamine and higher fatty acids.
5. Quaternary ammonium compounds containing a long-chain alkyl group.
6. Fatty acid esters of polyglycerols.

1. **Igepons** are condensation products between oleic acid and  $\beta$ -hydroxy or  $\beta$ -amino-ethylsulphonic acid. Their sodium salts have pronounced detergent properties. They are prepared by heating oleic acid with  $\beta$ -hydroxy- or  $\beta$ -amino-ethylsulphonic acid and converting the product to its sodium salt, *e.g.*,



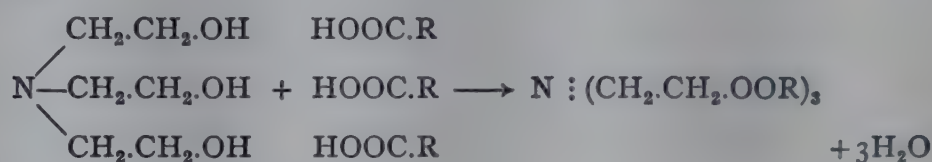


The amino-condensation product is completely stable to dilute acids and hard water whereas the oxy-condensation product is less stable to mineral acids.

2. **Salts of Monosulphuric Esters of Higher Fatty Alcohols.**—These alcohols can now be prepared technically by the catalytic hydrogenation at high pressure and temperature of the appropriate fatty acids or their esters (*e.g.*, hydrogen at 200°–250° C. and 100–200 atmospheres with a catalyst of reduced basic copper chromate). The alcohols thus produced are treated in practice with sulphur trioxide or sodium pyrosulphate in pyridine. The reaction mixture is diluted with water, exactly neutralising with caustic soda solution and salting out with brine.

3. **Alkyl Derivatives of Aromatic Sulphonic Acids.**—Twitchell first patented a method of using substituted naphthalene sulphonic acids as fat-splitting agents (artificial ferments). The sodium salt of isopropynaphthalene sulphonic acid is a valuable emulsifying and wetting agent.

4. **Salts between Triethanolamine and Higher Fatty Acids.**—These compounds are formed by esterification of triethanolamine by any of the higher fatty acids and have more pronounced wetting and emulsifying powers than ordinary soap.

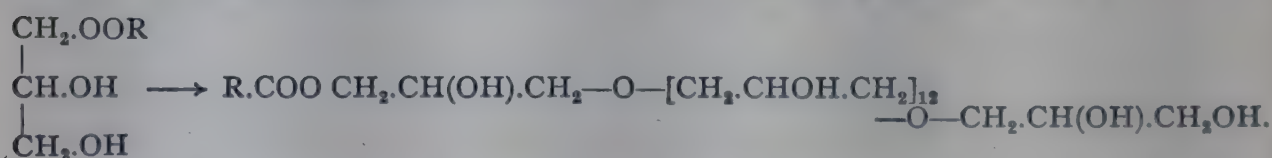


when R may be stearyl, oleyl, etc.

The products are used in shampoos and brushless shaving creams to emulsify castor oil, lanolin, etc., in these creams.

5. **Quaternary Ammonium Compounds containing a Long-chain Alkyl Group.**—These are such compounds as cetyltriethylammonium iodide —  $\text{C}_{16}\text{H}_{33}\text{N}(\text{C}_2\text{H}_5)_3\text{I}$  or CTAI. They are used as wetting and emulsifying agents in antiseptic creams, but have poor detergent properties.

6. **Fatty Acid Esters of Polyglycerols.**—These are compounds such as polymono-palmitin and polymono-olein formed by the polymerisation of



Glycerol is heated in the presence of suitable catalysts to produce the polyglycerol which is then heated with one molecular equivalent of fatty acid per molecule of polyglycerol.

These esters are non-dissociable compounds which are freely soluble in water and are not affected by hard water. They are hydrolysed by caustic soda. They are used particularly as emulsifying agents in margarine and cooking fats.

See T. P. Hilditch, "Industrial Fats and Waxes," for a fuller account (Baillière, Tindall and Cox, 1941).

### Some Improved Techniques

Graining out in a casual way, in which the quantity of salt used is not previously calculated, leads to the separation of the mass into curd and lye, but not always to the best advantage. The curd is contaminated with lye and the subsequent removal of glycerin is made incomplete. Experiments have shown that the amount of salt used in the graining process determines the amount of lye contaminating the curd. The best results are obtained when the quantity of salt added is no more than that required to precipitate the soap. It is thought that excess salt modifies the physical nature of the soap so that it tenaciously retains a portion of lye.



A calculation after the following principle is all that is really required. The soap in the pan is assumed to be all in the form of a hydrate containing 66 per cent. fatty acids and therefore the amount of hydrate is 1.52 times the weight of fatty acid present. After saponification the remaining contents of the pan can be assumed to be water and glycerin. Any salt present must be allowed for and more salt added in such a quantity that the total concentration is brought to that required for complete precipitation of the soap. For example, one ton of fatty acids give 1.52 tons of soap hydrate. The total weight of the contents of the pan after saponification will be 2.05 tons.  $2.05 - 1.52 = 0.53$  tons is the amount of water to which salt must be added to make a lye of the required composition. If this is 10 per cent., and the salt is in the form of 26 per cent. brine, it can be calculated that .33 tons of brine will be required. This deduction is usually made by means of a graph.

This scientific method of graining also ensures that the best recovery of glycerin is effected.

**The Strengthening Change.**—In the early days of soap manufacture the so-called strengthening change of caustic soda was used to ensure that complete saponification of the fats had taken place. Recent analyses of the curd have shown, however, that no measurable quantity of uncleansed fat need remain after the saponification charge. Large quantities of soap have been manufactured in recent years without the strengthening change, and no rancidity due to free fats has been reported.

The strengthening change has some definite disadvantages. The lye run off has to be used for saponifying fat in another pan. Such lyes have to be stored in a special tank. The strength of the lye may vary, and thus control is complicated. Lastly, the use of a strengthening change presupposes that the saponification is incomplete, so that an unconscientious soap-boiler may not bother particularly to complete the saponification before strengthening.

**Bleaching with Hypochlorite Solution.**—This is not an essential part of soap boiling, but is sometimes carried out when dark tallows and certain vegetable oils are being used. Hypochlorite cannot be used to bleach palm-oil soap, nor to bleach discoloured soap scraps. The reagent used is a 4 per cent. available chlorine one. This is prepared nowadays from chlorine gas in cylinders which is run into dilute caustic soda solution on a weighing machine, so that the correct strength may be judged by the increase in weight.

To carry out a bleach, the fat is saponified in the usual way and the soap washed at least once, which removes much of the oxidisable material which would otherwise use up some of the bleach. The soap is then boiled up with sufficient water to close up the curd. From a laboratory test, the amount of bleach required is estimated on a small sample and then the large batch treated by running in the calculated quantity of bleach into the boiling soap. The action takes place very quickly and when it appears complete (judged by treating a test sample with some more bleach) the soap is grained out. If the process has been properly carried out, the soap should not return to its original colour nor should it smell of chlorine.

**The Modern Fitting Technique.**—Although the old fitting process in which the appearance of the soap is judged by a high-skilled operator gives satisfactory results, there is a more scientific process in which the pan is weighed as water is added. That the old process requires considerable skill is evidenced by the fact that different soap bases require different quantities of water for fitting to bring about the same appearance when tested on the paddle.

The rational method is exactly the same as that described for making boils. The soap mixture in the pan is weighed by means of a gauge. Suppose the pan contains  $x$  tons of fatty acids and the curd to be fitted weighs  $y$  tons. Then  $x$  tons of fatty acids yield  $1.52x$  tons of soap hydrate (see under Graining Out, p. 102). Therefore  $y - 1.52x =$  weight of entangled lye. Suppose that this contains 10 per cent. salt and that a desirable type of fit is obtained by reducing this to 8 per cent. (the result of a previous boil). The final weight of free solution will be  $\frac{(y - 1.52x) \cdot 10}{8}$  tons, and the amount of water required for fitting, therefore, will be

$$\frac{(y - 1.52x) \cdot 10}{8} - (y - 1.52x) = (y - 1.52x) \left( \frac{10}{8} - 1 \right) \text{ tons.}$$

To carry out the operation the curd is boiled up with a little of the additional water to close it and the steam turned off when the soap rises to the top of the pan. The rest of the water is now gauged into the pan in small quantities at a time, boiling up between each addition until the whole of the required water has been added. There is no need to judge the end of the operation by the appearance of the soap and no highly-skilled labour is needed when the fitting is carried out by this scientific method. Very few additional laboratory tests are required. If we assume that the weight of fatty acids in the pan is known, the brine will contain 26 per cent. of salt if saturated, and weighing the curds and lyes will give all the information required to calculate the fatty acid and salt contents of the curd. By trial the salt concentration in the free solution which gives the required result is, of course, previously observed; but as long as the fat charge remains substantially constant this figure may be used for all future charges.



## XI.—GLYCEROL OR GLYCERIN \*

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### METHODS OF OBTAINING GLYCEROL FROM WASTE SOAP LYES

The waste lye as discharged from the soap kettle should contain 4-8 per cent. of glycerol, and be nearly neutral (0.04-0.4 per cent. NaOH are limits of alkalimetry), otherwise much valuable acid will be wasted in neutralising the excess of alkali. The greater the inferiority of the stock used in the manufacture of soap the greater will be cost of recovery of the glycerol present in the lye, both on account of the great amount of foreign organic matter present in the lye, which must be removed, and also because of the smaller amount of glycerol present in the stock.

Two systems are at present in vogue for glycerol recovery, namely:—

1. Van Ruymbeke's Process.
2. Garrigue's Process.

We will discuss each in turn.

#### Van Ruymbeke's Process of Glycerol Recovery

The waste lye reduced to its lowest practicable degree of alkalimetry, viz., under 0.4 per cent. NaOH, is run from the soap kettle to the storage tanks to cool; here any dissolved soap separates and heavy impurities sink to the bottom. The liquor is then run into the treating tank A (Fig. 41), made of sheet steel and provided with open steam pipes at the bottom for heating, and an air-jet for mechanical agitation. If the waste lye is strongly alkaline, either sulphuric or hydrochloric acid is run in until the liquor is almost neutral, and then basic ferric

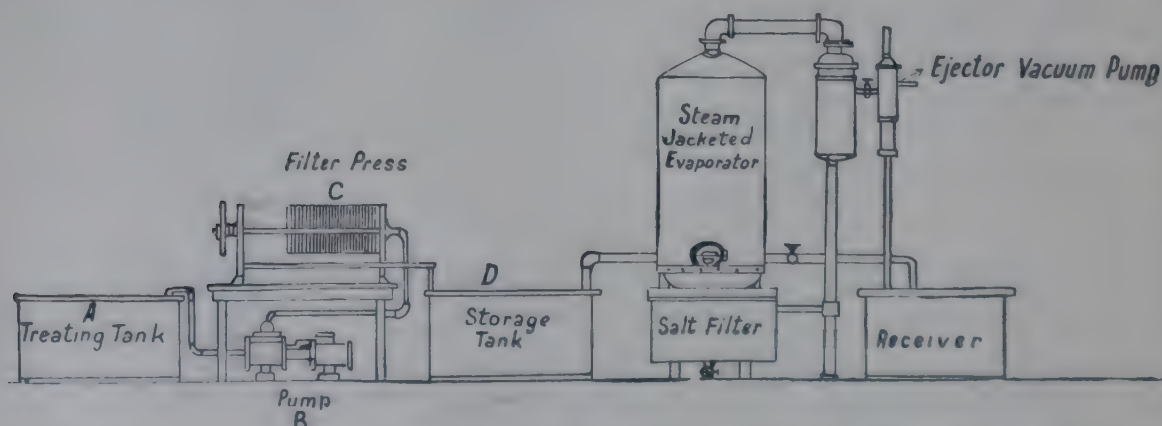


FIG. 41.—Van Ruymbeke's Process of Glycerol Recovery from Soap Lye.

\* The pure chemical product is termed “Glycerol” (which shows that it is an alcohol) while the impure commercial product is called “Glycerin.” Since this introduces an entirely superfluous complexity we will throughout the article use only the scientifically correct term, viz., glycerol.



sulphate solution added in the proper proportions. If, however, the liquid is only slightly alkaline the iron salt alone is used for neutralisation. Usually three-fourths of the alkali are neutralised by acid, and the remainder by the basic iron sulphate.

The iron salt is known as "Chemical sand," and is made by mixing a finely powdered and dried iron ore (analysing 50 per cent. iron oxide) with concentrated sulphuric acid (60° Be.) previously heated to 150° C. The mass is then run on to an iron floor, where the reaction continues and the mass solidifies. It is then broken up and heated for some hours at 200°-280° C. It then forms a mixture of ferric sulphate, ferric oxide, and a little free acid. Instead of this iron salt any of the alums may be used as a precipitant. They are, however, somewhat more expensive.

The acid added to the soap lye decomposes any soap present, setting free the fatty acids.

The iron salt then precipitates these acids as insoluble iron soaps, and at the same time carries down any albuminous matter (coagulated by heat).

The lye is then forced by means of the pump B through the filter press C, which retains the precipitated impurities, the lye flowing into another similar tank (not shown) where the process of purification is completed. The lye is then filtered off into the third tank D. It should now be clear, and possess a slight acid reaction. The exact amount of dry soda-ash to neutralise the liquor is now thrown in and thoroughly mixed, and the lye filtered from the resulting precipitate. It is then ready for evaporation in a "vacuum evaporator." This consists of a sheet-iron boiler heated internally by a series of steam pipes, while a vacuum pump maintains inside the vessel a vacuum of between 18 and 28 in. Under the diminished pressure the water boils off rapidly leaving the glycerol behind. In order to increase the effect sometimes two or three of these evaporators are used in series ("double"

or "triple" effect), the vapours from the first being used to heat the liquid in the second, and those of the second to vaporise the liquid in the third. In this way a greatly increased evaporative effect is obtained with the same amount of steam. As the liquid concentrates salt is deposited. It falls between the heating pipes of the boiler, and collects at the bottom, whence it is from time to time withdrawn through doors placed at the bottom of the vacuum chamber.

Fig. 42 shows a section of Foster's Waste Lye Evaporator.

The lye is boiled in the vessel A by means of the steam pipes B, the vapours rising up through C, which is connected with the vacuum pump. If the vessel is employed in multiple effect the hot

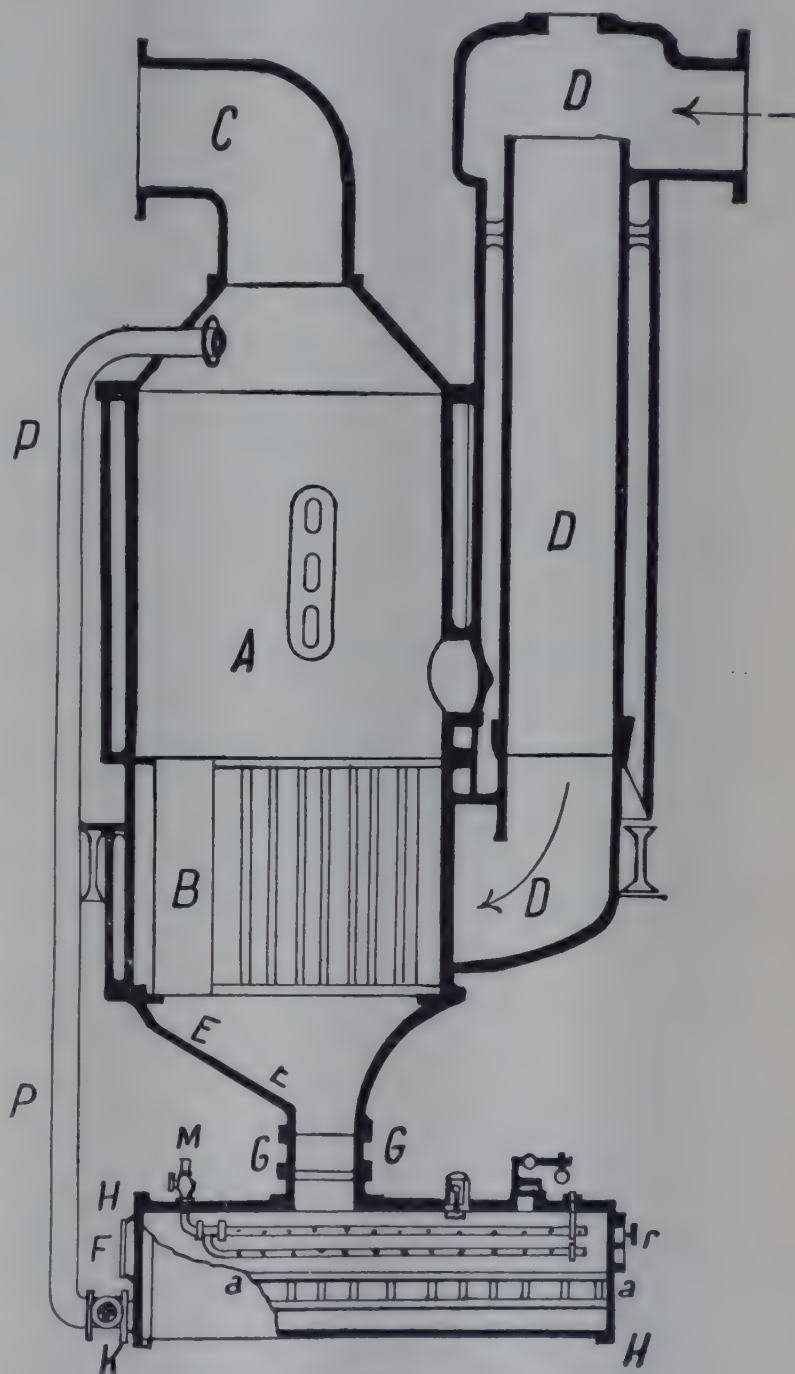


FIG. 42.—Foster's Waste Lye Evaporator.



vapours from the other vaporisers pass into the liquid by DDD, and help to maintain the evaporation, since the vacuum is greater in the second boiler than in the first, and so the vapours from the first boiler passing into the second are hot enough to maintain the liquid in it in rapid ebullition. The salt is deposited on the sloping hearth *EE*, and finds its way into the salt filter *HH*, the salt resting on a filter bed *aa* of iron netting and copper gauze placed over the gridiron plate. When the filter is filled with salt (which can be seen through the sight glass *F*) the valve at *G* is shut so that communication between the salt in *HH* and the vacuum in *A* is cut off; then the valve *K* is opened to the vacuum space in *A*, and a stream of steam is driven through *M* into the closed chamber, and drives the liquid through the salt in *HH*, the liquid and steam being sucked through *PP* into the top chamber *A*, leaving the salt on the filter *aa* quite dry. Then *K* is closed and the salt removed through a door *r*. The operations are therefore continuous, the salt being removed from time to time without breaking the vacuum. Usually two filter chambers are fitted to each evaporator, matters being so arranged that one is open to receive salt at the same time that salt is being removed from the other, so that a practically continuous withdrawal of salt takes place. Many other systems of evaporators (*e.g.*, Jobbins) are in use, all of which offer some special advantage. The salt separated is again used in soap graining. Fig. 43A shows a Kestner's patent desalting evaporator, which is used to an increasing extent for separating crystalline salts of all kinds from solutions.

The loss of glycerol by evaporation is extremely small when the operation is carried out under a vacuum of 26 in. and with steam at a low pressure. The liquid is boiled until a sample of lye withdrawn shows a density of 30° Be. at 15° C., when it consists of 50 per cent. glycerol, while most of the salt has been deposited and withdrawn. Then the liquid is sucked into a storage tank situated below the evaporator, allowed to cool, separated by filtration from any precipitated salt, passed into a second evaporator of a similar type but smaller, and the evaporation carried on until the proportion of glycerol reaches 80 per cent., the salts and water varying between 10 per cent. and 12 per cent. This glycerol is known as "Crude" and is now distilled.

**Distillation of Crude Glycerol.**—The still *A* (Fig. 43) consists of a steel boiler maintained at a high vacuum of 28 in. while its contents are heated by dry steam at 150° C. circulating through closed steam coil *aa*, while at the same time a current of live steam at 150° C. is blown through the glycerol by means of an open jet *bb*. This steam enters at *c*, passes down the tube *cde*, and suddenly expands to twenty or thirty times its original volume from the narrow tube *ef* into the wide steam coil *ggg*, which is placed in the steam heated chamber *BB* (felt-covered to avoid loss of heat) and which is filled with steam at 150° C. The steam in expanding from *ef*

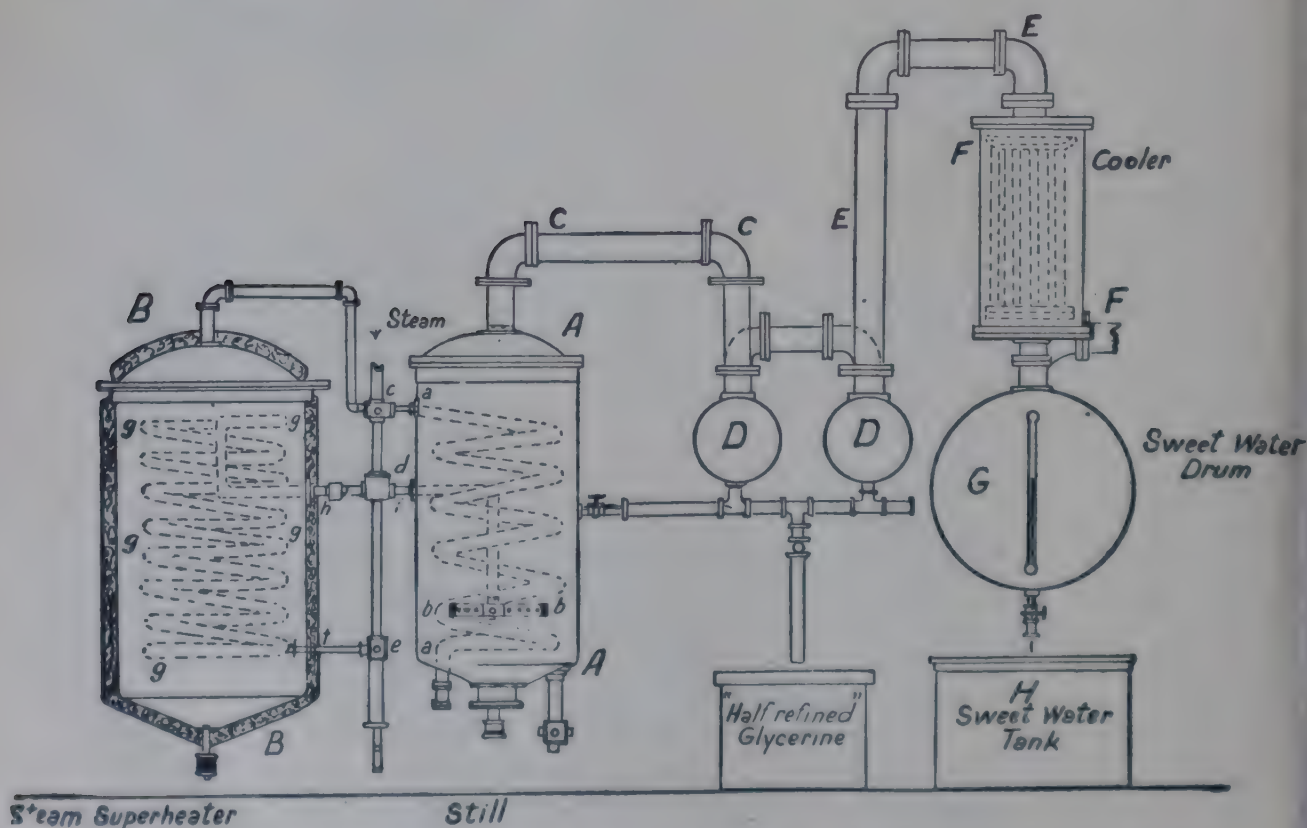


FIG. 43.—Jobbins Glycerol Distilling Apparatus.



# KESTNER'S PATENT DESALTING PLANT.

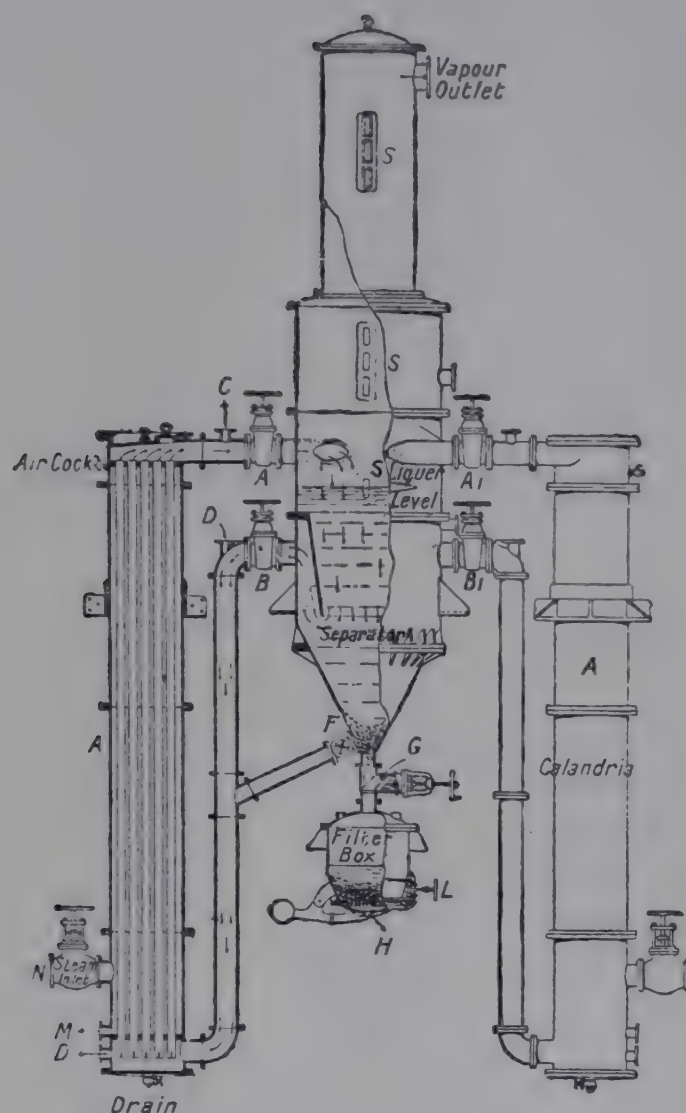


FIG. 43a.—Kestner Desalting Evaporator.

The separator ss is filled with liquor to above the opening B, the height of the liquor being seen through the sight glasses. The steam is turned on at N in the calandria A, which consists of a number of pipes running through a steam box, as shown in the drawing.

The liquor from the separator S then passes through B down into the bottom box of the calandria A, then boils up the tubes, and rushes back as vapour or liquid through A into the separator.

There thus takes place a continuous circulation of liquor through the separator and calandrias, and as crystals of salt form in the separator they fall down the central space formed by the circular baffle, any salt which crystallises out falling to the bottom of the cone, while the liquor passes through the outlet B, at which point it is practically free from salt. There may be as many as four calandrias connected to one separator, one being used for washing out or cleaning while the others are in action.

At the bottom of the separator is a valve G, by means of which accumulated salt is periodically run into the filter box, the valve G, being closed, the mother liquors run off at H, and the salt is removed from the box by means of the discharge door L.





into the wide coil *gg* has its temperature lowered, but the free steam at  $150^{\circ}\text{C}$ . in the superheater *BB* heats the expanded steam in the coil *gg* to its original temperature again, and this steam, in its expanded and dry condition, rushes through the pipe *hi* and blows in a dry hot stream through the jet *bb* into the glycerol in *AA* and causes it to distil rapidly, owing to the high vacuum maintained in *AA*, up through the pipe *cc*, into the drums *DD*, where practically pure glycerol collects ("half-refined"), while steam and the more volatile products pass away up the pipe *EE* through a series of pipes placed in a cooler *FF*, through which cold water circulates. Here the glycerol and steam are completely condensed and flow into the drum *G*, whence it is drawn off from time to time into the tank *H*. This latter distillate is known as "sweet-water" and contains a small amount of glycerol and volatile organic acids. It is worked up again for pure glycerol.

The level of the glycerol in the still *AA* is maintained constant during the distillation, liquid being continually admitted slowly to maintain the level constant as the liquid distils away. Finally there remains in *A* a considerable quantity of "glycerol foots," containing 30-50 per cent. of glycerol, which is recovered from it by a special process described below.

The "half-refined" glycerol which collects in *DD* is distilled once again and thus obtained pure.

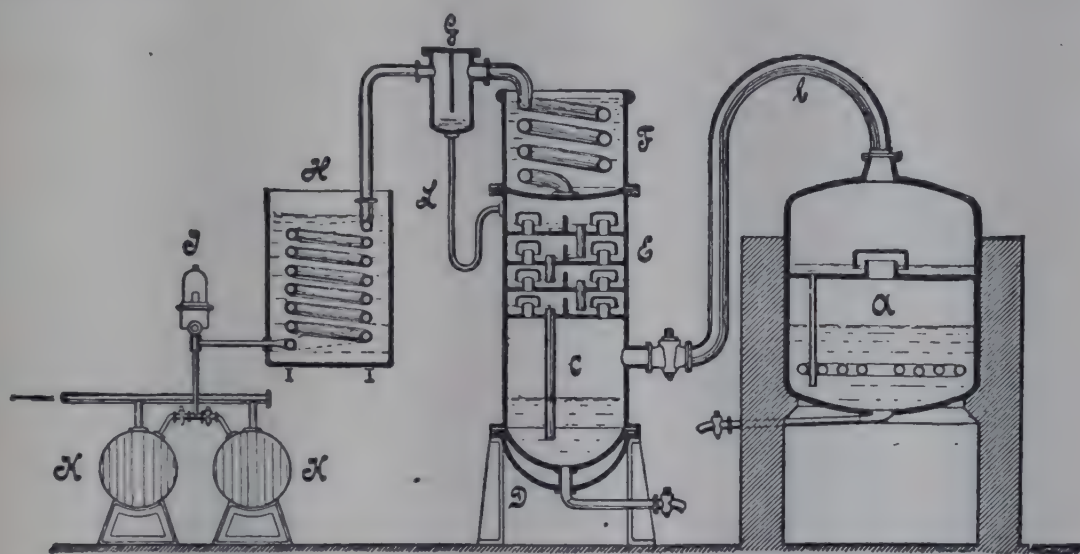


FIG. 44.—Heckmann's Glycerol Distilling Plant.

Fig. 44 shows a glycerol distilling plant designed by Heckmann, and much used in Germany. Glycerol is boiled in *a* by indirect steam, a high vacuum being maintained by a pump attached to *KK*, which lowers the boiling point of the liquid in *A* to about  $200^{\circ}\text{C}$ . The glycerol vapours and steam pass away through *G* into the rectifying column *CE*, to which is attached the *dephlegmator* *F*. The liquid condensing in *c* is maintained at about  $80^{\circ}\text{C}$ . by means of the steam-jacketed bottom *D*, so that the water scarcely condenses at all in this part of the apparatus, but passes away as steam, mixed with glycerol vapours, through the bell condensing trays in *E*, into the *dephlegmator* *F*, and finally reaches the catch-all *G*, where any condensed glycerol runs back through *L* into *C*, and is again distilled there. Consequently only concentrated glycerol collects in *C*, while steam and a very small amount of glycerol vapours pass over from *G* into the condenser *H*, the specific gravity of the water condensing in *H* being checked by a swimming hydrometer contained under a glass bell jar *J*. The glycerol in *C* is then withdrawn and decolourised with blood or animal charcoal (which has been carefully freed from mineral matter by extracting for weeks with  $\text{HCl}$  and washing with water).

**Concentration and Distillation of Sweet-Water.**—The sweet-water contains volatile organic acids, either free or combined with glycerol. It is therefore mixed with the exact amount of soda-ash to retain such acids in the "foots" as alkali salts. Next, the sweet-water is placed in the steel boiler *AA*, Fig. 45, provided with a steam heating coil *aa*; *cd* is a plate provided with a hole, at a short distance below which is another circular plate *ef* of slightly larger size, which prevents the liquid splashing up the tube *BB*, and consequently is known as the "dash plate." The valve *h* is closed, and a high vacuum is maintained in the concentrator *AA* by means of a vacuum pump connected with the receiving drum *D*. The liquid boils,



water vapour passes over through BB, and entering the catch-all CC, impinges against the tube *kl*, deposits the less volatile glycerol in the catch-all, while the water vapour, passing on, enters the tube *kl* and is deposited in the drum D. The glycerol deposited in CC is run back from time to time by means of *mn* into the concentrator AA.

When the glycerol in AA is sufficiently concentrated it is run into a Jobbins' distilling plant, previously described, and preferably made of tinned copper, and there finally distilled. It is finally concentrated to the proper specific gravity (1.262) and sold as "dynamite glycerol."

Refined glycerol is usually clarified by mixing a small quantity of bone-black with the hot liquid, and filtering. The product is of straw colour and is known as "dynamite glycerol." Colourless water-white glycerol is produced by a subsequent distillation and clarification of the dynamite refined grade.

**Utilisation of Glycerol Foots.**—The "foots" comprise the tarry residue left in the still in the distilling process. They contain from 30-50 per cent. of glycerol, 5 per cent. of salt, 20-30 per cent. of sodium acetate, and 10-15 per cent. of sodium salts of non-volatile fatty acids. The glycerol is removed by acidifying the mass with the exact amount of sulphuric acid necessary to combine with the sodium present—the sodium being estimated in a sample by incinerating and weighing as sodium

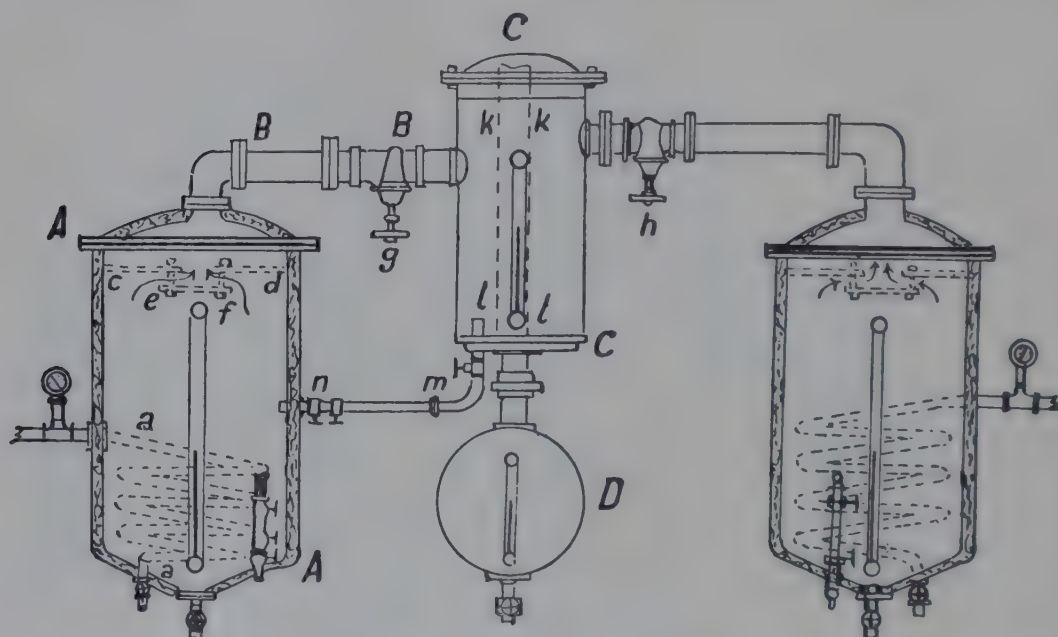


FIG. 45.—Plant for Concentrating Sweet-Water.

carbonate—in a lead-lined tank, and the darkened mass is, after standing, run through coarse filter bags and heated in an iron still, when the organic acids (principally acetic) volatilise. Finally the product is added to the waste lye direct from the soap kettle and worked up along with this for glycerol.

### Garrigue's Process for Glycerol Recovery

This method presents the following advantages over van Ruymbeke's process:—

1. In van Ruymbeke's system the volatile fatty acids (*e.g.*, acetic, butyric, caprylic, etc.) are imperfectly eliminated, distilling over with the glycerol even from an alkaline solution, and injuriously affecting the quality of the refined product. In Garrigue's system the volatile fatty acids are almost entirely eliminated *before distilling*.

2. In van Ruymbeke's system the presence of much alkali in the liquor to be distilled (added to the sweet-water in order to fix the fatty acids) greatly retards the distillation and does not effect complete separation, since some of the volatile fatty acids distil over with the glycerol, while some glycerol remains behind in the foots. In Garrigue's system so small an amount of alkali is used that it scarcely effects the distillation.

3. In van Ruymbeke's system considerable amounts of glycerol foots occur as residues in the still. These contain sometimes over 50 per cent. glycerol and cannot be economically discarded; the glycerol has therefore to be recovered by mixing with sulphuric acid as described above, and mixing the product with the raw material. Since the foots contain sodium salts of organic acids, these contaminate the glycerol. In Garrigue's system the foots produced are so small in quantity and so poor in glycerol that they can be discarded.



**Details of Garrigue's Process of Glycerol Recovery.**—The soap lye from the soap kettle is run into a storage tank, where any soap separates out and heavy impurities subside. Next it is run into the treating tank A, and there is added about 0.5 per cent. of aluminium sulphate (or common alum) and sufficient sulphuric acid to nearly neutralise the caustic soda and sodium carbonate present. The contents of the tank are agitated by means of air blown in from a Korting's exhaustor B through a perforated coil in the bottom of the tank. The sulphuric acid sets free the insoluble fatty acids before in the solution as soap, while the aluminium present at once precipitates them as insoluble aluminium soaps. After sufficient agitation, the liquid is forced by the pump C through the filter press D into the feeding tank E. The liquid is now clear. It then passes to the vacuum evaporator F and is concentrated (the level in the evaporator being kept constant by a continual introduction of lye in proportion as the liquid boils away). The concentration is carried on until the residual liquid contains about 40 per cent. of glycerol, and about 80 per cent. of the chloride and sulphate of sodium originally present in the liquor have crystallised out and been recovered in the usual way.

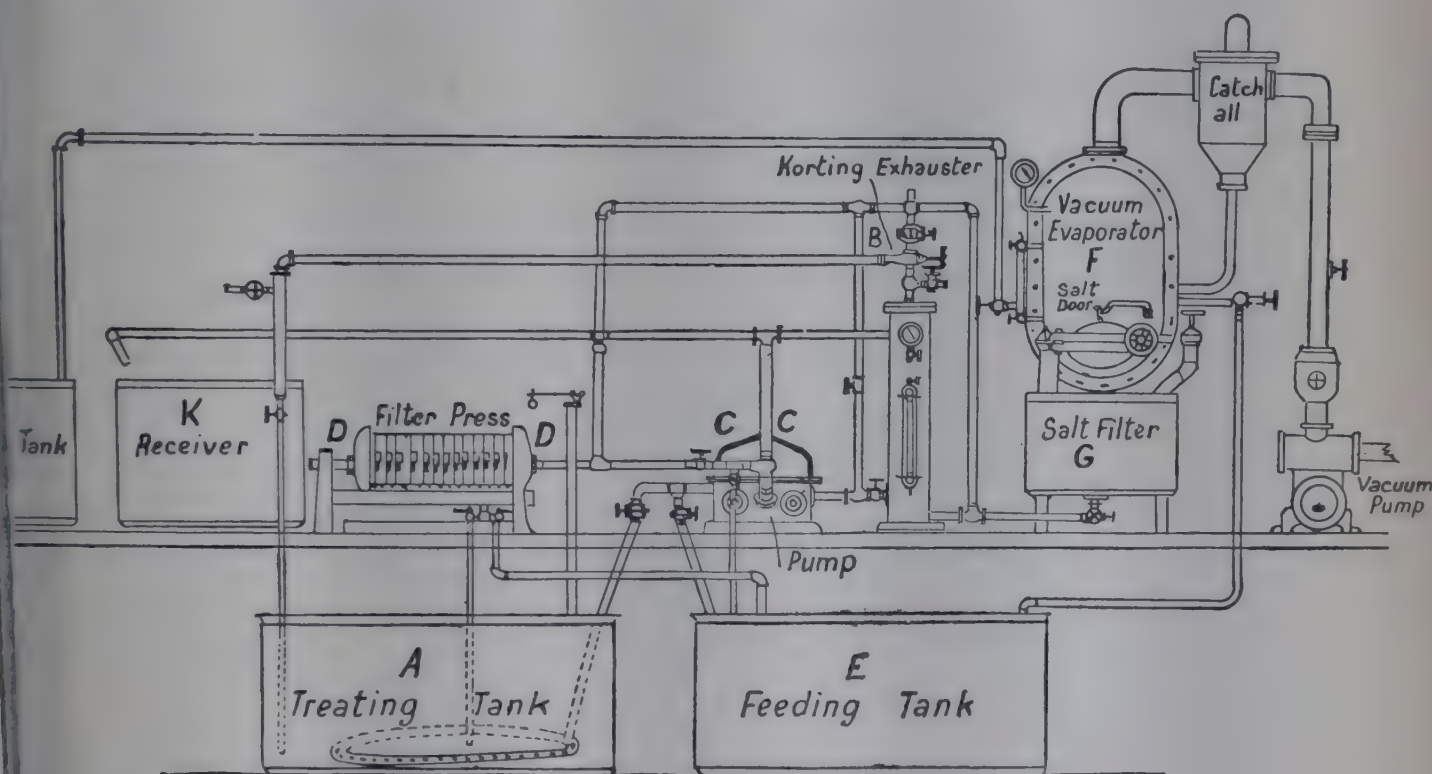


FIG. 46.—Garrigue's Process for Glycerol Recovery from Waste Soap Lye.

Next the liquid is allowed to flow from the evaporator F through the salt filter G (using a vacuum of 20 in. beneath the salt filter to force the liquid through), and is pumped away to the settling tank H.

So far the soluble and volatile fatty acids have remained in solution; these are now removed as follows. The concentrated liquor is pumped from the settling tank H into the treating tank A, and about 0.5 per cent. barium chloride,  $\text{BaCl}_2$ , stirred in. All the sodium sulphate remaining in the liquor is precipitated as barium sulphate, while any soap still present is decomposed and precipitated as an insoluble barium soap. Now sufficient sulphuric acid is added, sufficient to decompose all the alkali compounds of the volatile and soluble fatty acids, whereby the latter are set free, and in turn are almost completely precipitated as insoluble barium compounds, with the excess of barium chloride remaining in the liquid; thus the volatile acids are removed.

The amount of sulphuric acid required is estimated by withdrawing a sample of liquor, filtering it, weighing off 10 g. into a flask, adding 140 c.c. of distilled water, and 1 c.c. of concentrated sulphuric acid, connecting the flask with a Liebig's condenser, and distilling over 100 c.c. Finally,

this volume, which contains all the volatile acids, is titrated with standard caustic soda solution, using phenolphthalein as indicator. The organic acidity is then calculated in terms of sulphuric acid, and then the necessary charge of sulphuric acid for the total amount of crude liquor is calculated and run in.

After a thorough agitation the liquid is filtered through the filter press D, Fig. 46, into the feeding tank E, and is thence pumped into the evaporator F, and concentrated until

the level of the liquor in the gauge glass remains constant. The volatile fatty acids still remaining (for they are not completely precipitated by the barium chloride) are in part expelled with the water vapour, but part remains to combine with the glycerol as the concentration proceeds, and are retained by it in the form of glycerides. Finally, when the concentration has proceeded so far that the liquid contains 85 per cent. of glycerol, it is discharged from the evaporator F into the receiver K, and is tested for total acidity by adding excess of standard alkali to a measured sample of the hot glycerol, heating, and titrating back the excess of alkali with standard sulphuric acid. This gives the measure of organic acids still present. The amount of a saturated solution of sodium carbonate (soda-ash) required for neutralisation is now calculated, and added to the crude glycerol in the receiver K, the amount being sufficient to render the mass slightly alkaline. The crude glycerol is now distilled.

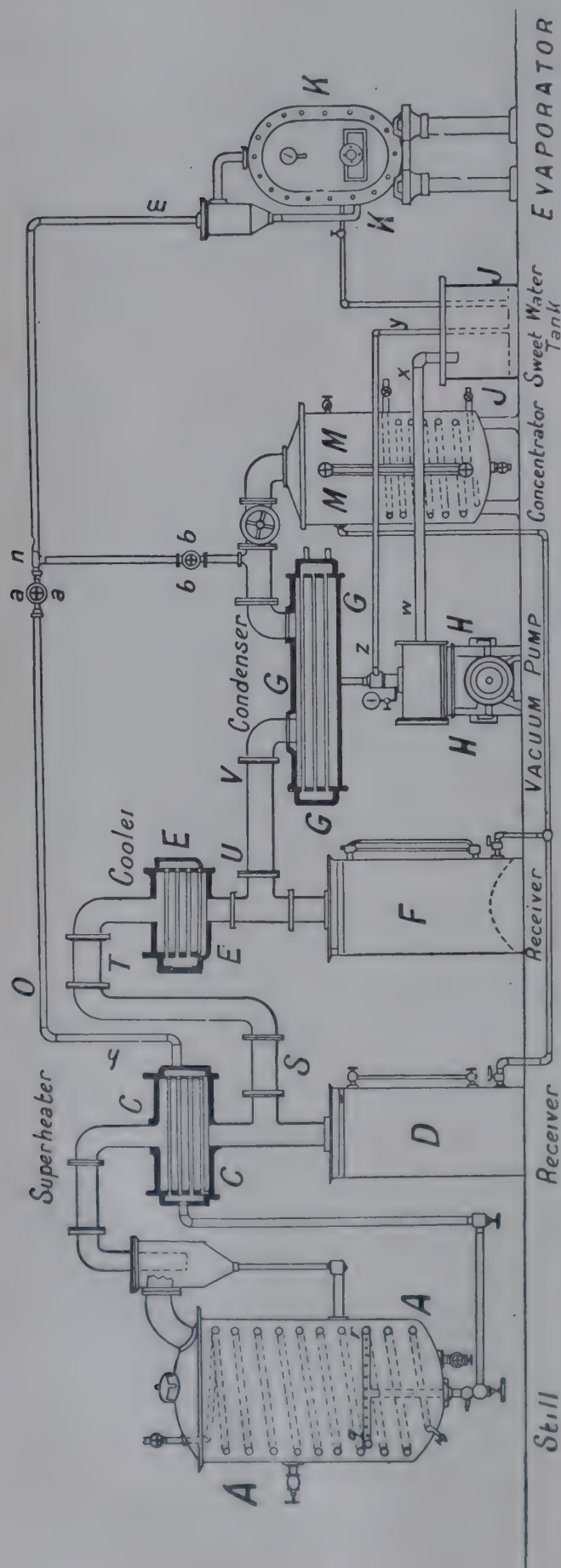


FIG. 47.—Garrigue's Plant for Distilling Glycerol.

**Garrigue's Process for Distilling Glycerol.**—Fig. 47 shows a complete Garrigue's plant for glycerol distillation. A is the still in which the crude glycerol is heated to about  $163^{\circ}\text{C}$ . by a closed steam coil, while a vacuum pump H maintains a vacuum of about 28 in. Under these circumstances the glycerol rapidly distils. K is an evaporator, filled with "sweet-water" from a previous distillation. This glycerol water is heated by closed steam coils in the evaporator (the steam used is low pressure direct from the exhaust of the vacuum pump H), while a vacuum of about 22 in. is maintained within the vessel. Under these circumstances the





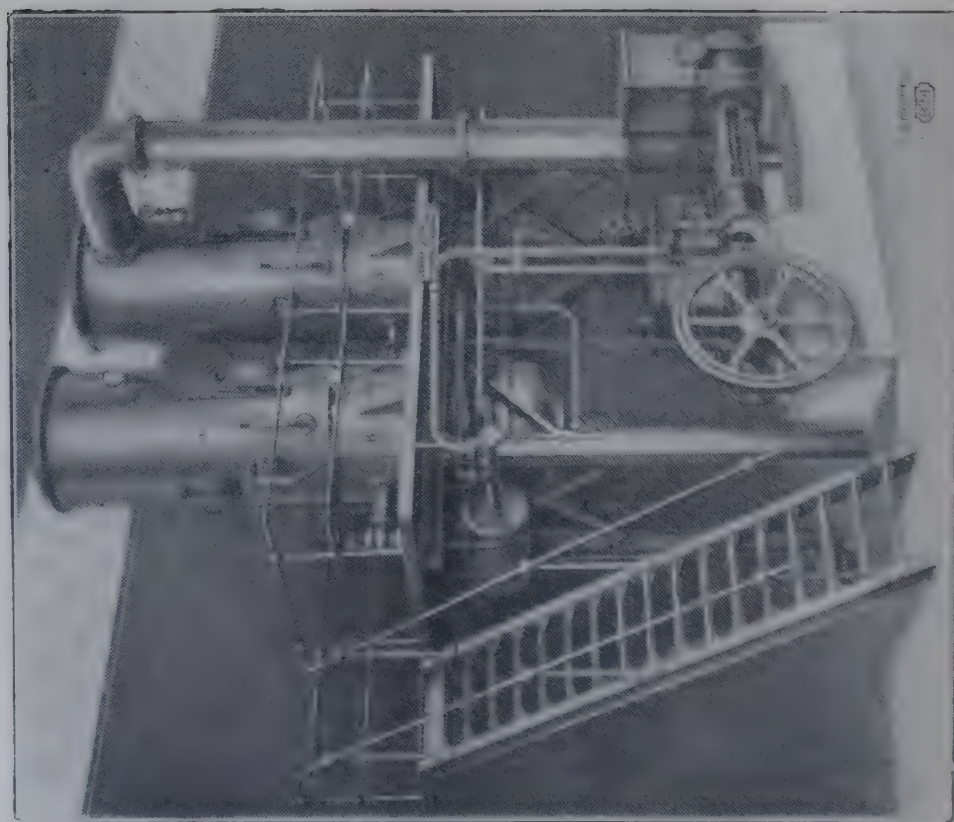


FIG 47A.—Scott Double Effect Glycerine Evaporating Plant,  
Salting Type.

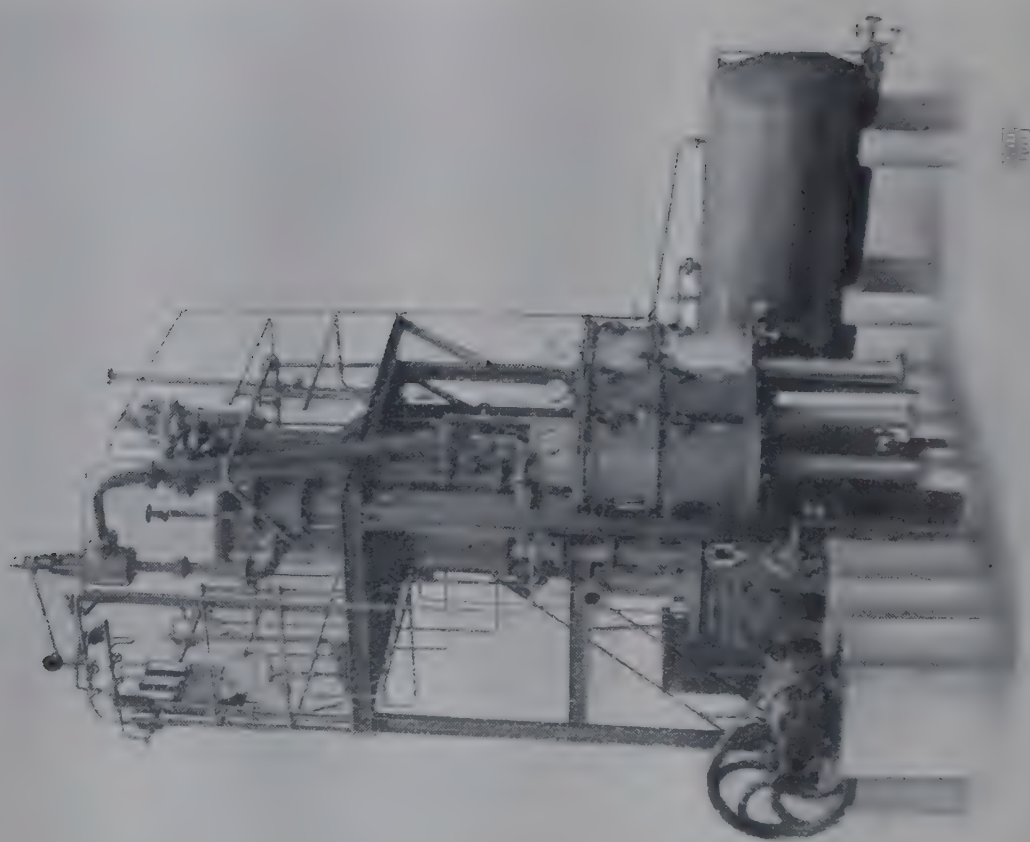


FIG. 47B.—Scott Patent High Vacuum Glycerine Distillation Plant.



glycerol water rapidly boils, and a current of steam at a temperature considerably below  $100^{\circ}\text{C}$ . is driven along the pipe *mnop*, and rushes through a series of tubes running through the centre of a chamber *c* (the "superheater"), which is filled with hot glycerol vapours at about  $160^{\circ}\text{C}$ . on their way from the still *A* to the receiver *D*. Here a double action occurs. On the one hand the cooler pipes conveying the steam from *K* serve to condense the glycerol, while on the other hand the hotter glycerol vapours serve to heat the pipes, and consequently the sweet-water vapours become greatly superheated to a temperature of about  $160^{\circ}\text{C}$ ., and blow rapidly in this dry superheated condition through the perforated coil *qr* into the boiling glycerol in the still, and aids its distillation. The abstraction of heat from the vapour of the distilling glycerol where it meets the steam pipes in *c* causes a large part of the glycerol to condense on the tubes of the superheater, and thence drop into the first receiver *D*. This glycerol is a finished product, being almost water-white, with a density of 1.263. A large proportion of the glycerol vapours, however, pass on up the tube *st*, and enter a chamber *E*, called the "Glycerol Cooler." Through this chamber run a number of tubes conveying hot water, which, entering at a temperature of about  $66^{\circ}\text{C}$ ., and leaving at about  $88^{\circ}\text{C}$ . (being heated in its passage by the hot glycerol vapours condensing on the tubes), causes the glycerol alone to condense and drop into the receiver *F*, while the steam passes on into the condenser *G*.

The glycerol condensed in *F* has a sp. gr. of about 1.250. It is not advisable for all the glycerol to condense in *F*, otherwise the volatile fatty acids which have escaped elimination in the crude glycerol evaporator would also condense and impart to the glycerol in *F* a too high acidity. Consequently matters are so arranged that about 3 per cent. of the total glycerol passes on with the steam through *uv*, and enters the sweet-water condenser *GG*. Here it enters a chamber filled with copper pipes carrying a stream of cold water, and consequently almost all the steam and glycerol condense to sweet-water, which, pouring down through the vacuum pump *H*, are passed by the tube *wx* into the sweet-water tank *JJ*.

Usually the sweet-water does not condense in quantity sufficient to keep the pump *H* properly sealed, and so it is usual to have a small return pipe *yz* from the open sweet-water tank to the pump suction, so as to allow some of the sweet-water to maintain a continuous circuit through the pump.

In the best practice matters are arranged so that about 2 lbs. of steam are injected into the still for every pound of glycerol distilled. Since the sweet-water should contain about 3 per cent. of the total glycerol, it follows that it should have a glycerol content of about  $1\frac{1}{2}$  per cent.

From the sweet-water tank *J* the sweet-water is fed continuously (being sucked in by means of the vacuum) into the evaporator *K*. The glycerol content of the sweet-water in *K* continually increases as the distillation proceeds, and at the same time there is a continual increase in the volume of sweet-water in circulation. When the glycerol in the evaporator *K* reaches about 25 per cent., it is run into the concentrator *MM*, and evaporated until the concentration becomes 80 per cent. glycerol. Since all the volatile acids gradually accumulate in the sweet-water, this concentrated glycerol must be returned to the still for redistillation. Towards the close of the operation the still *A* is shut off by closing the valve *aa*; the valve *bb* is opened, and the glycerol in *KK* is concentrated until it reaches 80 per cent. The aqueous vapours condensed from this concentration are run to waste through the vacuum pump.

In some works the contents of the sweet-water concentrator *K* are emptied from time to time into the settling tank of the crude glycerol plant, and fed with the rest of the glycerol into the still as required for distillation.

While distilling it is best to maintain the feed of crude glycerol at a constant level, just above the perforated jet-pipes, during the whole time of distilling (twenty-four hours). The charge then left in the still is run into the waste lye treatment tank, where the colouring matter is removed by chemical means as previously described.

Figs. 47*a* and 47*b* illustrate how the principles described above are adopted in modern plant. For a fuller description of modern plant the reader is referred to Martin's "The Manufacture of Glycerol" which deals entirely with glycerol.

**Uses of Glycerol.**—By far the greater part of glycerol is used for making nitroglycerine; besides this it is used as a sweet conserving fluid for preserved



fruit, as a lotion or basis for ointments, in gas meters and hydraulic jacks to prevent freezing, for lubricating moulds, for preventing shrinkage in wooden vessels, in clay modelling, in artists' colours, in calico printing, in cements and inks, in photography, to impart elasticity to leather and paper, etc. Glycerol is sometimes (illegally) added to alcoholic drinks as an unfermentable and harmless sweetener.

**Properties of Glycerol.**—When pure, it is a solid, M.P.  $20^{\circ}\text{C}$ ., but as usually obtained it is a sweet tasting, thick liquid, colourless, of sp. gr. 1.265 at  $15^{\circ}\text{C}$ ., and B.P.  $290^{\circ}$  at 760 mm. (with slight decomposition),  $210^{\circ}\text{C}$ . at 50 mm.,  $179.5^{\circ}\text{C}$ . at 12.5 mm.,  $163^{\circ}\text{C}$ . at 10 mm. It does not volatilise at ordinary temperatures, but when heated at  $100^{\circ}\text{C}$ . a slight loss occurs, especially in the presence of steam. Heated with dehydrating agents it changes into acrolein, thus—



When pure, glycerol ignites at  $150^{\circ}\text{C}$ ., and burns gently with a pale blue flame without odour or residue.

Dynamite glycerol must have a minimum sp. gr. of 1.262, contain no  $\text{CaO}$ ,  $\text{H}_2\text{SO}_4$ , or  $\text{Cl}$ , not more than 0.1 per cent. of ash, and must not reduce  $\text{AgNO}_3$  solution. Glycerol derived from decomposing fats frequently contains trimethylene glycol,  $\text{C}_3\text{H}_6(\text{OH})_2$ , which lowers the boiling point and specific gravity.

At  $160^{\circ}\text{C}$ . glycerol dissolves two-thirds of its weight of boric acid, forming glyceryl borate,  $\text{C}_3\text{H}_5\text{BO}_3$ , which is used as a preservative ("boro-glyceride"). Glycerol is miscible in all proportions in water and alcohol, sparingly soluble in ether (1,000 parts ether dissolve  $2\frac{1}{2}$  glycerol) and in ethyl acetate, 100 parts of which dissolve 9 of glycerol; glycerol is insoluble in chloroform, petroleum ether, benzene, and carbon disulphide, also in oils and fats. Glycerol is an excellent solvent, many substances dissolving in it with greater ease than in water or alcohol; thus it dissolves 98 per cent. soda crystals, 60 per cent. borax, 50.5 per cent. potassium arsenate, 50 per cent. zinc chloride, 40 per cent. alum, 40 per cent. potassium iodide, 30 per cent. copper sulphate, 25 per cent. ferrous sulphate, 25 per cent. potassium bromide, 20 per cent. lead acetate, 20 per cent. ammonium carbonate, 20 per cent. arsenious oxide, 20 per cent. arsenic acid, 20 per cent. ammonium chloride, 15 per cent. oxalic acid, 10 per cent. barium chloride, 10 per cent. copper acetate, 8 per cent. sodium bicarbonate, 7.5 per cent. mercury bichloride, 5 per cent. calcium sulphite, 3.5 per cent. potassium chlorate, 1.9 per cent. iodine, 1 per cent. calcium sulphate, 0.7 per cent. iron oleate, 0.9 per cent. magnesium oleate, 1.18 per cent. calcium oleate. Glycerol also dissolves caustic alkalis, alkaline earths, and lead oxide, and in the presence of caustic alkalis also ferric oxide, cupric oxide, and bismuth oxide.

**Glyceryl Phosphoric Acid**,  $\text{C}_3\text{H}_5(\text{OH})_2\text{O}.\text{PO}(\text{OH})_2$ .—Formed by mixing  $\text{P}_2\text{O}_5$  with glycerol, and known only in aqueous solution (20-50 per cent.). Dibasic acid. Salts used medicinally, having a strong action on the nervous system. In this form phosphorus is rapidly assimilated. **Tonal** is the name given to preparations of its salts, **kalio-tonal** being potassium glyceryl phosphate.

**Statistics.**—The world's production of glycerol amounts to 80,000 tons. Germany produces about 10,000 tons. England imported in 1910 about 4,000 tons, of value £230,000; she exported 11,900 tons, of value £653,000. The United States imported in 1910 41,182,000 lbs., of value \$3,666,000. For modern statistics see Appendix III.

**Detection and Estimation of Glycerol.**—To detect glycerol dry the substance thoroughly at  $100^{\circ}\text{C}$ ., mix with twice its weight of finely powdered potassium hydrogen sulphate, and heat (on the sand bath) in a small flask fitted with a leading tube passing into a test-tube placed in a freezing mixture. In the presence of glycerol the characteristically smelling acrolein will be evolved, the presence of which may be confirmed by adding to the liquid in the test-tube a few drops of a mixture of 3 g. of silver nitrate in 30 g. ammonia (sp. gr. 0.923), and 3 g. of sodium hydroxide in 30 g. water. A silver mirror should rapidly appear.

**Estimation of Glycerol in Fats.**—The glycerol is separated from the fat by saponifying with alcoholic  $\text{KOH}$ , filtering the soap solution, setting free the fatty acids by  $\text{HCl}$ , and filtering them off. The aqueous extract, containing all the glycerol, is neutralised with  $\text{BaCO}_3$ , evaporated, and the glycerol extracted with ether. On evaporating the ether the crude glycerol is left and may be weighed. A weighed portion of this glycerol is acetylated in the usual way with acetic anhydride and dried sodium acetate, the excess of acetic acid *exactly* neutralised with  $\text{NaOH}$  in the cold, and the number of acetyl groups in the  $\text{C}_3\text{H}_5(\text{OC}_2\text{H}_3\text{O})_3$  determined by adding *excess* of standard  $\text{NaOH}$ , and boiling and titrating back with acid. From the equation—



it will be seen that 3 molecules of  $\text{NaOH}$  used up denote 1 molecule of glycerol present. The amount of glycerol in the whole may then be estimated. This method cannot be used for waste soap lye and other products low in glycerol. It gives somewhat low results.



**Estimation of Glycerol in Soap Lyes.**—250 c.c. of soap lye is acidified with  $\text{H}_2\text{SO}_4$ , the fatty acids filtered off, lead acetate added, the precipitate filtered off, the solution evaporated, made up to 100 c.c., and 25 c.c. are boiled thirty seconds with 25 c.c. concentrated  $\text{H}_2\text{SO}_4$  and 40 c.c.  $\text{K}_2\text{Cr}_2\text{O}_7$  solution containing 75 g. per litre. From the equation—



it will be seen that for every 1 g. of glycerol oxidised 7.5 g. of dichromate disappear. The exact strength of dichromate before and after boiling is found by titrating with ferrous ammonium sulphate in the ordinary way. From the loss in strength of the dichromate the amount of glycerol can be calculated. The results are usually too high.

For a critical survey of other methods of glycerol estimation the reader is referred to Allen's "Commercial Organic Analysis," Lewkowitsch's "Chemical Technology and Analysis of Oils, Fats, and Waxes," or Wright-Mitchell's "Oils, Fats, and Waxes."

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## XII.—ESSENTIAL OILS

BY THE LATE C. AINSWORTH MITCHELL, B.A., F.R.I.C.

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The volatile essential oils, which are produced in numerous plants, differ from the fixed oils in many important particulars.

Most essential oils are mobile odoriferous liquids which, as a rule, may be distilled without undergoing decomposition, and usually they are composed of several constituents, in one or more of which the characteristic aroma of the oil is concentrated.

In some plants the essential oil is contained in the blossoms, while the rest of the plant contains little or none. In other plants, such as those that produce spices, the bulk of the oil may be in the root or bark; whilst in others, again, essential oil, in proportions varying with the stage of growth, occurs in all the organs of the plant.

Various methods of separating the oil are in use, the choice depending upon the nature of the oil and the quantity that can be extracted.

Thus in preparing scents from flowers the petals are heated in stills containing water, the steam carrying over the volatile oil into the condenser.

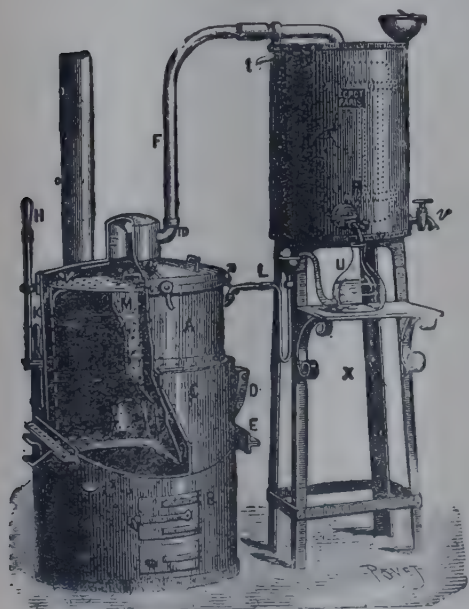


FIG. 48.—Perfume Still.  
(Manufactured by Egrot, Paris.)

Fig. 48 shows a still of this kind much used in France. It consists of a still A placed over a fire B. Inside A is a perforated copper basket M containing the flowers. The still is nearly filled with water, which, boiling, carries over the essential oil with the steam through F into the condenser R. The water and oil as it condenses discharges into the Florentine vase U, the essential oil usually collecting on the surface of the water, whence it is drawn off from time to time. The condensed water runs back through L into the boiler.

In the larger modern stills the steam is introduced from an outside boiler, and as the temperature and pressure can thus be better regulated there is less risk of overheating oils of delicate aroma.

In separating oils from lemon and orange peel and other products containing a large proportion of essential oil mechanical methods of expression are commonly employed, and distillation with steam is only used for separating an inferior grade of oil from the residues.

The rinds of such fruits as *limes*, *lemons*, *oranges*, *bergamots* are rich in essential oils—the so-called *citrus* oils—and much attention has been directed in recent years to expressing those oils



economically from them, an object all the more important as those rinds are, to a great extent, a waste product. The following are recent English Patents:—13,171, 1904; 6,036, 1909; 15,552, 1909.

An extraction method with a volatile solvent such as alcohol, or with olive oil or lard, is used in the preparation of delicate scents, the essential oils being subsequently separated from the extracts.

A typical modern extraction plant (Egrot's, of Paris) is shown in Fig. 50. The volatile solvent (alcohol, ether, benzene, carbon bisulphide) is raised by the pump into the collector D, which is provided with a glass gauge tube by means of which the volume of the contained liquid may be ascertained. The basket G, filled with plants, is lowered by means of tackle into the extractor A, which is then closed. Next the solvent from D is run into the heater E, containing a steam worm, and, according to its density, is thence sent into the extractor A either from above (by the pipe  $b'$ ) or from below (pipe  $b$ ), and comes out again by one of the pipes  $c$  or  $c'$ , after which, charged with perfume, it goes into the evaporator B by the pipes  $d$  and  $f$ . Here in B a heating coil vaporises the solvent, which passes as a vapour up the tube  $g$  into the condenser C and thence into the collector D, where it re-enters into circulation. The perfume remains behind in B. Finally the solvent is distilled off from the exhausted flowers in A. If alcohol is used as a solvent it soon becomes diluted with the moisture contained in the flowers. Consequently the alcohol is distilled away from A through a rectifier F, which only allows a sufficiently alcoholic distillate to pass. This is condensed in C and collected in D and used again; after which A is opened and the basket withdrawn and replaced by a basket filled with fresh flowers.

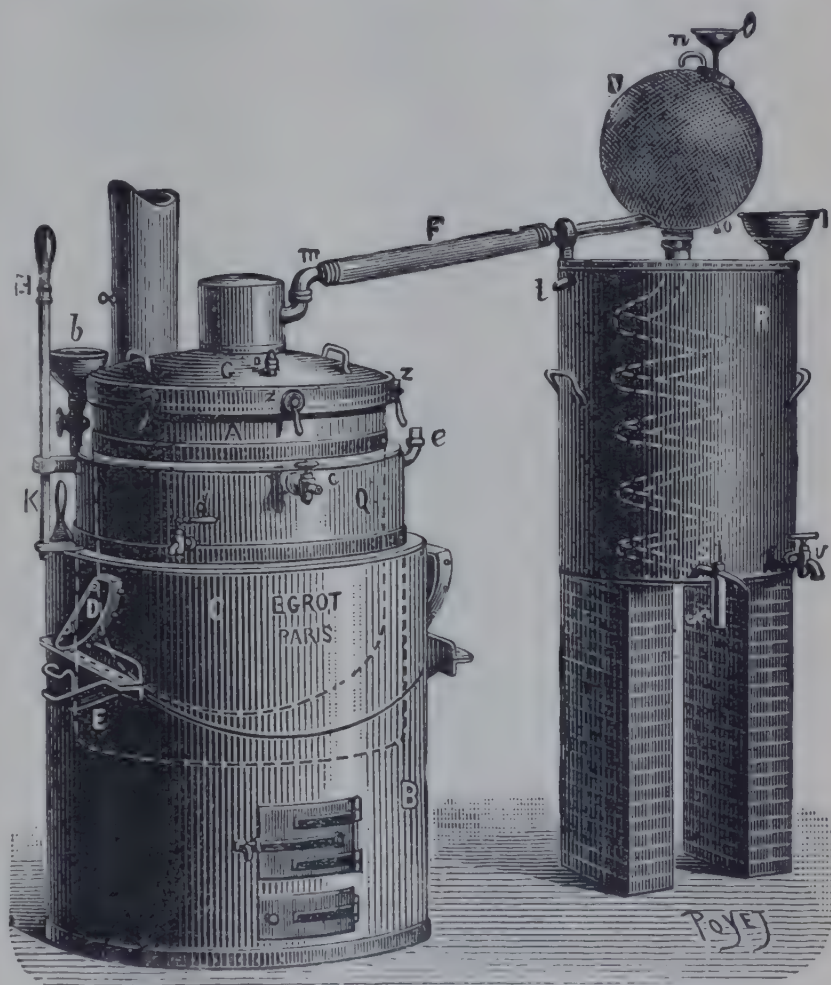


FIG. 49.—Perfume Still. (Egrot, Paris.)

### Characteristics.—

Essential oils differ widely from one another both in properties and composition, and it is not possible to classify them into distinct separate groups, as in the case of the fixed oils and fats.

Some are colourless, while others are green or dark brown in colour. In most cases they are lighter than water, but a few, like oil of cinnamon, are heavier. In some cases they readily undergo oxidation upon exposure to air and light; and hence it is usual for the manufacturers to send out orange or lemon oils in copper vessels the top of which is sealed with solder.

Frequently an essential oil is made up of several fluid constituents, while in other cases solid compounds (the so-called *stearoptenes*) are present in solution, and can be separated by chilling the oil. "Otto" of rose may be cited as an instance of this kind.

A high refractive index is a characteristic of essential oils, and its determination is one of the most important means of ascertaining the purity of an oil.

The compounds that have been isolated from essential oils include the hydrocarbon series known as terpenes, having the composition  $C_{10}H_{16}$ ; alcohols and ketones related to the terpenes, such as borneol,  $C_{10}H_{17}OH$ , and camphor,  $C_{10}H_{16}O$ ;



compounds typified by the alcohols, geraniol and citronellol; phenols and their derivatives; and aliphatic derivatives.

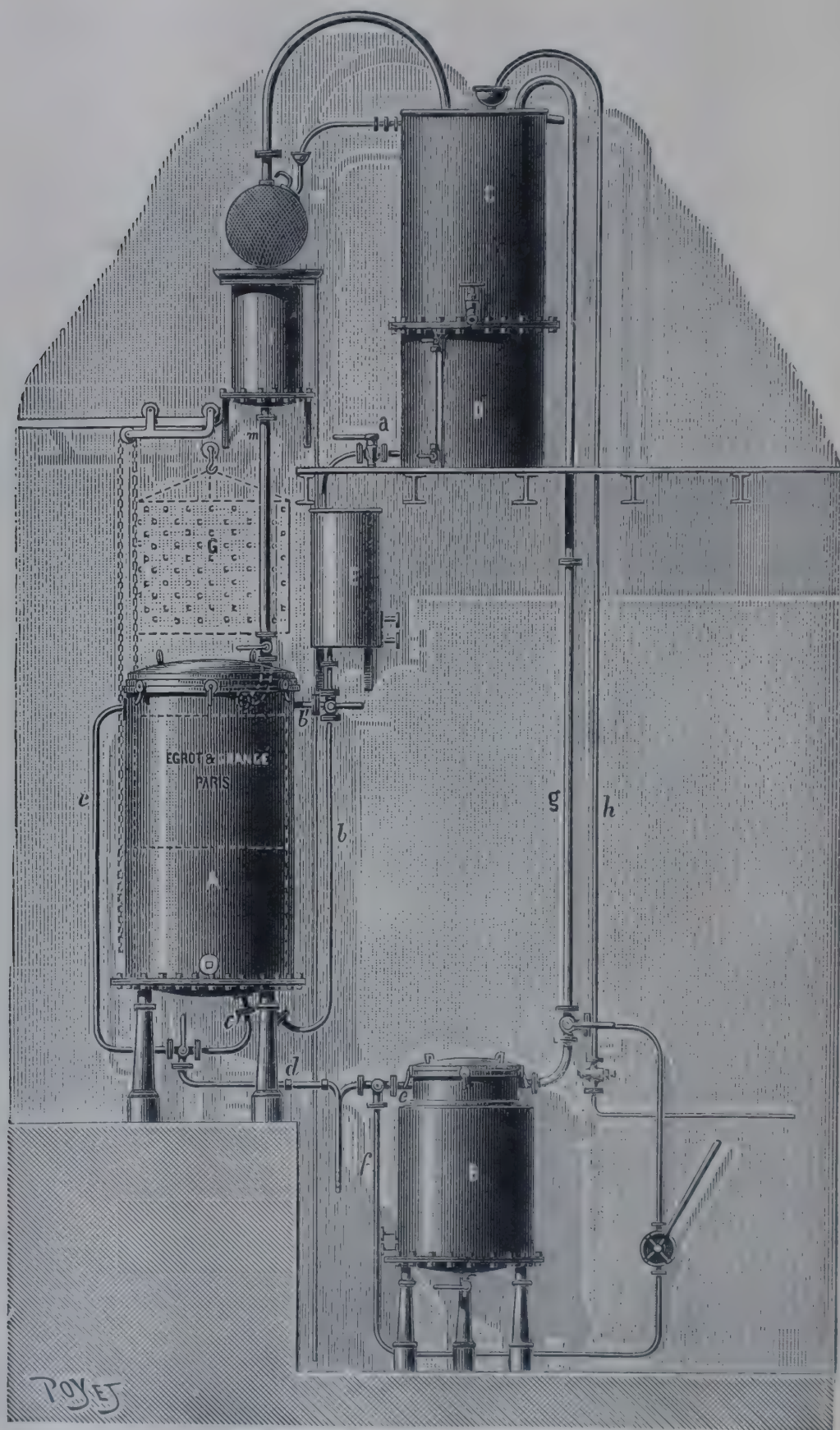


FIG. 50.—Extraction Plant for Essential Oils. (Egrot, Paris.)

**Analysis of Essential Oils.**—The estimation of the quantities and proportions of special compounds in an essential oil is of great importance in certain cases in which it pays to separate the active constituent and to sell it separately, and also



in the detection of adulteration when an oil containing a certain compound is mixed with another which does not contain it.

For instance, Japanese peppermint oil contains upwards of 80 per cent. of menthol, and a large proportion of this is frequently separated by a process of freezing, leaving only about 30-35 per cent. in the so-called "dementholised" oil, which is accordingly sold at a considerably lower price, and often used to adulterate untreated peppermint oils.

Again, clove oil should contain over 70 per cent. of the compound, eugenol, and should the proportion be much lower than this, the addition of an adulterant, such as oil of turpentine, is suggested; or a portion of the eugenol may have been removed and sold separately.

The essential oils which contain characteristic compounds, the estimation of which may afford data as to purity, include the following important products:—

Citronella oil (containing citronella); lemon-grass oil (containing citral); sassafras oil (containing safrol); bergamot oil (containing linalyl acetate); peppermint oil (containing menthol); (clove oil containing eugenol); lemon oil (containing citral); aniseed oil (containing anethol); oil of camphor (containing safrol); and eucalyptus oils (containing eucalyptol).

In addition to estimating the characteristic constituents of an oil, where this is applicable, the various physical properties are also determined, and the oil is separated by fractional distillation into several fractions which may then be further examined.

The specific gravity of essential oils may show great variations, as for example:—

Aniseed oil	-	-	-	0.9852	Clove oil	-	-	-	1.047
Bergamot oil	-	-	-	0.8808	Rose oil	-	-	-	0.8912
Lemon oil	-	-	-	0.8498	Turpentine oil	-	-	-	0.873

Thus an addition of, for instance, turpentine oil to clove oil would reduce the specific gravity below the normal figure.

The optical properties usually determined are the refractive index and the specific rotation. For instance, clove oil has a specific rotation of about  $-4^{\circ}$ , while turpentine oil often has a rotation as high as  $-75^{\circ}$ .

Again, lemon oil has a pronounced dextro-rotatory power (about  $+60^{\circ}$ ), whereas lemon-grass oil is nearly inactive in this respect ( $+3^{\circ}$  to  $-3^{\circ}$ ).

The solubility of an oil in certain solvents is in many cases a useful test. Thus citronella oil should dissolve completely in two to three times its volume of 80 per cent. alcohol at  $20^{\circ}$  C., whereas an oil containing paraffin oil, which is a common adulterant, is much less soluble.

The use of the distillation method is valuable, *e.g.*, in the examination of lemon oil, which is very frequently adulterated with oil of turpentine. Now since the latter has a considerably lower boiling point it can be concentrated in the first tenth of the distillate, and then detected by determining the optical activity of this fraction.

One of the most difficult adulterants to detect is an addition of terpenes, *i.e.*, the residual fraction left in the manufacture of so-called *terpeneless oils*. The latter are products made, for instance, from lemon oil by removing the inert substances (the terpenes) so that an oil with a much more concentrated flavour is obtained. Prepared oils of this kind are used in the mineral water industry, and give an improved flavour which more than compensates for the increased cost.

In cases where the residual terpenes have been used to adulterate, *e.g.*, lemon oil, the physical properties of the oil might be made so nearly normal as to make the oil seem genuine.

The adulteration of certain oils used in perfumery, such as rose oil, may also be done so skilfully that reliance must in the last resort be placed upon the judgment of a specialist who can discriminate between the odour of a genuine and an adulterated product.

**Statistics.**—The quantity of essential oil imported into the United Kingdom is shown below. Figures are also given showing the value of the *artificial* essential oils. (For these see next article by Dr Martin on *Synthetic Perfumes*).

	1908.	1910.	Value in 1910.
	Lbs.	Lbs.	
Natural essential oil	1,841,300	1,983,000	£320,000
Artificial essential oil	163,400	169,600	34,400

The United States in 1910 imported 415,000 lbs. of essential oils, of value \$309,383. The export in the same year was 110,000 lbs. of *peppermint oil* (value, \$216,000), and \$322,000 value of other sorts. For modern statistics see Appendix III.



## XIII.—SYNTHETIC PERFUMES

BY G. MARTIN, Ph.D., D.Sc.

## LITERATURE

See under "Essential Oils."

Within recent years certain synthetic perfumes of great technical importance have been placed on the market. Perhaps the most important are **Ionone** (odour of violets) and **Vanillin** (aromatic principle of vanilla). Although most perfumes can be prepared synthetically from coal-tar products, yet in many cases they are merely separated in a pure state from less costly natural oils, sometimes by fractional distillation, and sometimes by other chemical actions. Thus, phenols, for example, are separated from aldehydes and ketones by their capacity for dissolving in caustic alkali; aldehydes and ketones (*e.g.*, citral) are separated by causing them to unite with sodium bisulphite; while sweet-smelling alcohols (*e.g.*, geraniol) may be separated by causing them to unite with anhydrous calcium chloride, or by esterifying them with dibasic acids and dissolving out the resulting esters with alkaline carbonates. The volatile products thus isolated are purified by distillation, the solid by crystallisation from organic solvents.

The scent industry has received a powerful impetus from synthetic scents, and Germany now turns out annually scents to the value of £2,000,000. The majority of the natural odours of flowers are due to complex mixtures of different scents. Almost all of these scents have been successfully reproduced by mixtures of synthetic scents, ranging from that of the violet to that of the rose. Although natural oil of roses contains about twenty different odorous substances, yet chemists employed by the German firms of Heine & Co., Schimmel & Co. (Leipzig) have succeeded in isolating all the components, synthesising these or preparing them from less costly oils, and then reuniting them in the proper proportions.

Synthetic attar of roses is now on the market.

Similarly **ionone**—an enormously powerful scent—is the basis of all violet-like scents.

In 1910 England imported 169,599 lbs. (=75.7 tons) of artificial essential oils, worth £34,370. Of this Germany contributed 140,000 lbs. (82 per cent.). The natural essential oils imported had a value of £320,000, and a weight of 900 tons.

The following are the chief synthetic (simple) perfumes, many of which occur naturally in essential oils :—

## Alcohols

**Citronellol**,  $C_{10}H_{20}O$ .—Artificially made by reducing citronellal. Occurs in rose and geranium oil. Used for making artificial **Rose Oil**. B.P., 224-227.

**Geraniol**,  $C_{10}H_{18}O$ .—Isolated from palmrosa citron oil. Used as soap perfume, and for artificial rose oil. B.P., 230-232.

**Linalol**,  $C_{10}H_{18}O$ .—Isolated from linaloe oil, and used as a substitute for linaloe oil. B.P., 199-200.

**Benzyl Alcohol**,  $C_6H_5.CH_2OH$ , from benzaldehyde by reducing also by treating benzyl chloride with lead hydroxide and water. Used as a constituent of perfumes.

**Phenylethyl Alcohol**,  $C_6H_5.CH_2CH_2OH$ .—Prepared by reducing phenyl-acetic acid,  $C_6H_5.CH_2.COOH$ . Occurs in rose water and rose oil. Soluble in water. Used in producing a rose scent.

**Cinnamic Alcohol**, **Styryl Alcohol**,  $C_6H_5.CH:CH.CH_2OH$ .—Isolated from storax. Hyacinth odour. M.P., 33°; B.P., 255.



**Menthol**,  $C_{10}H_{19}OH$ .—Isolated from Japanese peppermint oil by freezing out; forms needles. M.P.,  $44^{\circ}$ ; B.P.,  $216$ . Used for peppermint oil, and in medicine.

**Terpineol**,  $C_{10}H_{17}OH$ , occurs naturally in different ethereal oils, and is produced artificially by reducing **Pinene**. Important constituent of many perfumes. Odour of hyacinths, hawthorn, or lilac.

**Santalol**,  $C_{15}H_{25}OH$ .—Isolated by fractional distillation from sandal-wood oil. Used in medicine and perfumery.

### Aldehydes

**Citral**,  $C_9H_{15}CHO$ .—Isolated from lemon-grass oil. Used as a lemon aroma, and for manufacture of ionone. B.P.,  $227-229$ .

**Citronellal**,  $C_9H_{17}CHO$ .—Isolated from the oil of the *Eucalyptus maculata*, var. *citriodora*. Used in perfumery.

**Benzaldehyde**,  $C_6H_5CHO$  (oil of bitter almonds, etc.).—Used as a soap scent. Manufactured on large scale. See p. 429.

**Anis-aldehyde**,  $C_6H_4(OCH_3)CHO$  (1:4).—Prepared by oxidising anethol,  $C_6H_4(OCH_3)C_3H_5$ , or by methylating *p*-oxybenzaldehyde. B.P.,  $244^{\circ}C$ . Hawthorn scent. Soap perfume.

**Heliotropin, Piperonal**.—Prepared from isosafrol by oxidation. Yellow crystals. M.P.,  $36-37$ . Heliotrope scent. Soap perfume.

$$C_6H_5 \begin{array}{c} \diagup CHO \\ \diagdown O \end{array} \begin{array}{c} (1:3:4) \\ \diagup O \\ \diagdown O \end{array} CH_2$$

**Vanillin**,  $C_6H_3(CHO)(OCH_3)(OH)$  (1:3:4), occurs naturally in the vanilla pod and is prepared synthetically on the large scale by oxidising isoeugenol or eugenol, by introducing an aldehyde group into guaiacol, and by methylating proto-catechualdehyde. M.P.,  $82^{\circ}$ . Used for perfuming food, and as a substitute for vanilla.

**Phenylacetaldehyde**,  $C_6H_5CH_2CHO$ .—Prepared by reducing phenylacetic acid, and from cinnamic acid. B.P.,  $210^{\circ}C$ . Hyacinth odour. Soap perfume.

**Cinnamic Aldehyde**,  $C_6H_5CH=CHCHO$ , occurs in various oils; prepared by condensation of benzaldehyde with acetaldehyde. B.P.,  $125^{\circ}$  at 15 mm. Substitute for cassia oil.

### Ketones

**Carvone**,  $C_{10}H_{14}O$ .—Isolated from caraway, dill, and spearmint oils. Used for beverages, etc.

**Ionone**,  $C_{13}H_{20}O$ .—Synthetically prepared by condensing citral with acetone by means of alkalies and then treating with acids. B.P.,  $243-246^{\circ}C$ . Most important "Violet" scent.

$$\begin{array}{c} CH_3, CH_3 \\ \diagdown \quad \diagup \\ C \\ \diagup \quad \diagdown \\ H_2C \quad CH \cdot CH : CH \cdot CO \cdot CH_3 \\ \diagdown \quad \diagup \\ H_2C \quad CH \\ \diagup \quad \diagdown \\ CH \\ \text{Ionone.} \end{array}$$

### Phenols and Phenolic Esters

**Carvacrol**,  $C_{10}H_{14}O$ , and **Thymol**,  $C_{10}H_{14}O$ , are isolated parts of various essential oils.

**Anethol**,  $C_6H_4(O.CH_3)(C_3H_5)$ , occurs in oil of anise seed and other oils. Separated by freezing out. M.P., 21; B.P., 235. Important perfume.

**Eugenol**,  $C_6H_3(OCH_3)(C_3H_5)(OH)$ .—Isolated from oil of cloves by treating with KOH. Used for making **Vanillin**, also as a perfume for beverages. **Iso-eugenol** is isomeric with eugenol and is easily converted into it by alkalis.

**Safrol**,  $C_{10}H_{10}O_2$ .—Isolated on industrial scale from **sassafras oil** and used for making **Heliotropin**, also as a soap scent.

**Nerolin**,  $C_{10}H_7.OCH_3$ ,  $\beta$ -naphthol-methyl-ether; smells somewhat like pine-apples. Soap perfume.

### Oxides

**Cineol**,  $C_{10}H_{18}O$ , occurs in numerous ethereal oils. B.P., 177° C. Camphor-like odour. Cosmetic and soap perfume.

### Fatty Acid Esters

See under Fruit Essences, p. 382. Important besides are—

**Geranyl Acetate**, **Linalyl Acetate**, **Borneol Acetate**, and **Amyl Salicylate**.—Methyl ester of anthranilic acid and homologues.

### Lactones

**Coumarin**,  $C_6H_4 \begin{array}{c} \diagup O \diagdown \\ C_2H_2 \end{array} CO$ , occurs in Tonquin beans, and is synthesised by Perkin's reaction from salicylic aldehyde and acetic anhydride. Important perfume.

### Miscellaneous

**Allylisothiocyanate**,  $C_4H_5SN$ , is the active constituent of mustard oil, and is manufactured by distilling allyl iodide with alcoholic potassium thiocyanate,  $CN.SK + C_3H_5I = CS.N.C_3H_5 + KI$ . B.P., 151° C.

**Artificial Musks** are nitrated tertiary butyl alcohols made by various processes (see English Patents, 18,521, 1888; 4,963, 1889), but have no chemical relationship to real *musk*, whose odour is due to a ketone,  $C_{15}H_{28}O$ , of unknown constitution.\* Soap and toilet perfume.

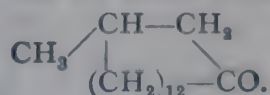
**Indol**,  $C_8H_7N$ .—Prepared from indigo, and used for making synthetic **Jasmin oil**.

**Nitro-benzene**,  $C_6H_5NO_2$ , is sometimes used instead of benzaldehyde, the odour being somewhat similar. See pp. 422, 429.

**Exaltone** (cyclopentadecanone) is now used in perfumery. This is a synthetic musk perfume of the above type.

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\* Recent views (Paul Karrer) are that the odour of musk is due to a ketone (muscone)





## SECTION II

### The Sugar Industry





# THE SUGAR INDUSTRY

## I.—SUGAR

BY G. DRUCE LANDER, D.Sc., F.R.I.C.

Revised by J. L. FERGUS, A.H-W.C., A.R.I.C.

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 C. A. BROWNE.—“A Handbook of Sugar Analysis.” New York.  
 See under Starch for literature relating to Dextrin and Glucose.

In the following account of the technology of sugar no more can be attempted than to convey an idea of the chemical considerations, so far as they are known, which underlie the various steps; and to indicate the special chemical engineering problems which had to be solved in order to obtain the modern high percentage of extraction from the natural juices. For details as to the numerous precautions and special points which have to be scrupulously observed in practice, reference may be made to the excellent special manuals of the subject.

SUGAR to the chemist is the general name of a numerous group of organic compounds containing carbon, hydrogen, and oxygen, the group being a division of the larger family of carbohydrates.

The chief classes of sugar are: The **Monosaccharides**, *pentoses*,  $C_5H_{10}O_5$ , represented by arabinose and xylose; *hexoses*,  $C_6H_{12}O_6$ , represented by glucose, fructose, and galactose. The **Disaccharides**,  $C_{12}H_{22}O_{11}$ , represented by sucrose, maltose, and lactose. The **Trisaccharides**,  $C_{18}H_{32}O_{16}$  represented by raffinose, only those of technological importance being mentioned. All the sugars are colourless, odourless, crystalline substances, usually of sweet taste, for the most part easily soluble in water, and are of vegetable origin, except lactose, which is the sugar present in the milk of mammalian animals. Numerous synonyms for the common sugars are in use and may give rise to confusion. They are:—

Sucrose	-	-	-	cane sugar, saccharose, or sugar.
Glucose	-	-	-	dextrose, grape sugar.
Fructose	-	-	-	levulose, fruit sugar.
Lactose	-	-	-	milk sugar.
Maltose	-	-	-	malt sugar.

In technology "sugar" means **Sucrose**,  $C_{12}H_{22}O_{11}$ , whether derived from the sugar cane, beet, palm, maple, or sorghum.

### SUCROSE (CANE SUGAR, BEET SUGAR, ETC.), $C_{12}H_{22}O_{11}$

**Properties.**—Sucrose crystallises in colourless crystals belonging to the monoclinic system, and has hemihedral surfaces. The sucrose may take up soluble colouring matter during crystallisation. Specific gravity at  $15^\circ C.$  is 1.591. It is extremely soluble in water, a saturated solution, at  $20^\circ C.$ , containing 67.09 grams per 100 grams of solution.

The boiling-points of aqueous sucrose solutions of different concentrations is given by Geerlach, as follows:—

Per cent. sucrose	-	10	20	30	40	50	60	70	80	90.8
Boiling-point $^\circ C.$	-	100.4	100.6	101.0	101.5	102.0	103.0	106.5	112.0	130.0

For the rapid analysis of the fairly pure sugar, specific gravity is taken by Brix hydrometers in the cane sugar industry, and by Balling hydrometers in the beet sugar industry, which indicates the percentage by weight of sucrose in a pure sugar solution. In industrial use it is usual to consider the degree Brix as the percentage of solid matter, or the total solids, dissolved in a liquid. The Brix hydrometer reads  $0^\circ$  at  $20^\circ C.$  in distilled water, according to the standard adopted by the International Congress of Chemistry. The Balling hydrometers are not, however, used in density determinations of crude beet juices, due to the presence of foreign extract matter.

The solubility of sucrose is affected by the presence of foreign substances. Such impurities retard crystallisation and prevent the crystallisation of sugar from molasses in the sugar factory. This is known as the melassigenic action of salts and has been explained by Geerligs as being due to a combination between the invert sugars and the mineral organic salts (mainly potassium salts) in the molasses. If invert sugar is present in only small quantities, any remaining mineral salts form sucrose salt complexes, thus preventing the complete crystallisation of the sucrose.

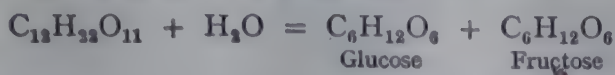
Sucrose is dextro-rotary, having a specific rotation in aqueous solution of  $\alpha_D^{20} = +66.5$ .

When dry, sucrose melts without decomposition at  $160^\circ C.$ , but enters incipient decomposition even at  $100^\circ C.$  when moist, giving at the melting-point, glucose and fructosan ( $C_6H_{10}O_5$ ); at  $170^\circ C.$  to  $190^\circ C.$  by loss of water, the



dark coloured caramel is formed, whilst at higher temperatures it finally carbonises, giving off carbon monoxide, formic acid, and other products.

On boiling sucrose in solution it is gradually hydrolysed or inverted—



—more rapidly under pressure. This inversion is favoured by metals and hindered, by reason of alkalinity, by glass. Acids accelerate inversion in proportion to their dissociation constants, sugar being rapidly inverted in warm solutions by mineral acids, less rapidly by organic acids. Salts effect inversion if they suffer hydrolytic dissociation according to the nature of the metal and acid. Thus sulphates of zinc and copper, being acid, cause inversion, whereas salts of strong bases with weak acids do not cause inversion, and may by mass action check the inversion due to other salts.

Sucrose forms sucrates with alkalis, such as  $\text{C}_{12}\text{H}_{21}\text{O}_{11}\text{K}$ , which are alkaline and decomposed by  $\text{CO}_2$ . The sucrates of lime and strontia are of importance in technology. The mono- and disucrate of lime are soluble in water at normal temperature, decomposed by  $\text{CO}_2$ , and on boiling give insoluble tribasic sucrate



which, when suspended in water, is also decomposed by  $\text{CO}_2$ .

Sucrose is acted on by many ferments:

#### (1) Bacteria :

- (a) Species which destroy sucrose, without the formation of gums.
- (b) Species such as *Leuconostic mesenteroides*, which forms gums from sucrose in dilute solutions.
- (c) Species known as *Thermophilis*, which develop at temperatures from  $45^\circ\text{C}$ . to  $70^\circ\text{C}$ . and sometimes cause decomposition of clarified juices.

#### (2) Mold Fungi :

- (a) Species such as *Aspergillus repens*, a strongly inverting type found in dilute and concentrated solutions.
- (b) Species such as *Monilia fusca*, with feeble inverting power and usually active at  $80^\circ$  to  $90^\circ$  Brix.
- (c) Species such as *Monilia nigra*, very common in sugar products but with weak inverting powers.

#### (3) Yeasts :

Species found in raw juices and which induce active inversion.

**Production of Sugar.**—The only sources of great commercial significance are from the juices of the cane and sugar beet. The sugar palm, date, sorghum, and maple are worked for sugar which, however, chiefly finds local use. As regards distribution, cane is a tropical plant, or sub-tropical, indigenous to India, and beet is a temperate zone crop, although sugar beet has been grown in the same locality as cane.

**Sugar cane** contains on an average 11–17 per cent. sucrose, 0.4–1.5 per cent. reducing sugars, 0.5–1.0 per cent. ash, and 10–18 per cent. fibre. Other constituents are nitrogenous bodies (amido acids, nitric acid, and xanthin bodies), 0.3–0.6 per cent. waxes, and pectins.

**Sugar beet** contains 13–18 per cent. sucrose and 5 per cent. non-sugar constituents (ash, nitrogenous matter, pectin, dextrine, raffinose, etc. The weight of roots per acre varies from 10–16 tons, but some countries cannot get more than 6 tons. Usually a high yield of roots per acre is accompanied by a low sucrose content.

The yield of cane per acre varies from 5 to as much as 100 tons per acre.



The stages in the technical extraction of sugar may be divided into (1) preliminary treatment, (2) preparation of dilute extract by expression or solution, (3) purification or removal of extraneous organic matter (gums and proteins), (4) concentration to thick syrup, (5) boiling to "grain," (6) crystallisation, (7) centrifuging, (8) drying and grading (see Figs. 51*b* and 51*c*).

The latter stages of this series (4-8) are alike for cane and beet. The operations 1-3 will be outlined for the extraction from beet first.

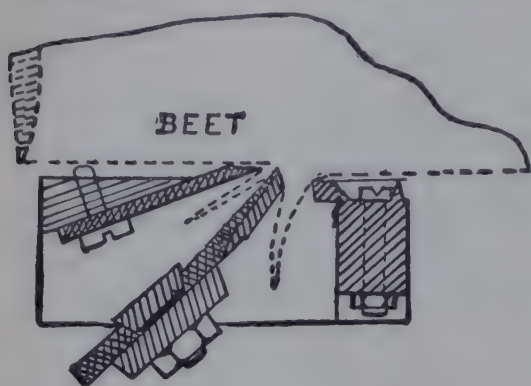


FIG 51.—Section of Beet Slicing Knife.

agitates them and drives them forward, stones sinking, and lighter impurities being removed by the reverse water current.

More compact machinery is sometimes used, for example in Raude's system, in which the roots are fed into a vertical cylinder of water in which helices are working. They sink, are driven to the periphery, and then upwards by the screws to the exit, from which they are taken on an endless screw. The cleansing in such cases is caused by the rubbing of the roots together, and requires that the machine shall be kept full.

The beets are then sliced. They are fed into a hopper from which they pass on to a horizontal circular disc carrying knives by which they are cut into slices.

The most usual form is V-shaped, like the ridge tile of a roof, a form which tends to prevent close packing, a desirable point in the subsequent diffusion. The discs vary from 1.2-2.5 metres in diameter. The knives are fixed into holders, which can be easily taken off or fixed, and it is of great importance that they should be very keen, so as to give well-cut slices.

**2. The Preparation of a Solution—Diffusion.**—Expression of the juice has been abandoned now for many years in the beet industry. The diffusion process (Robert, 1860) takes advantage of the phenomenon of osmosis through the cell wall. When immersed in water,

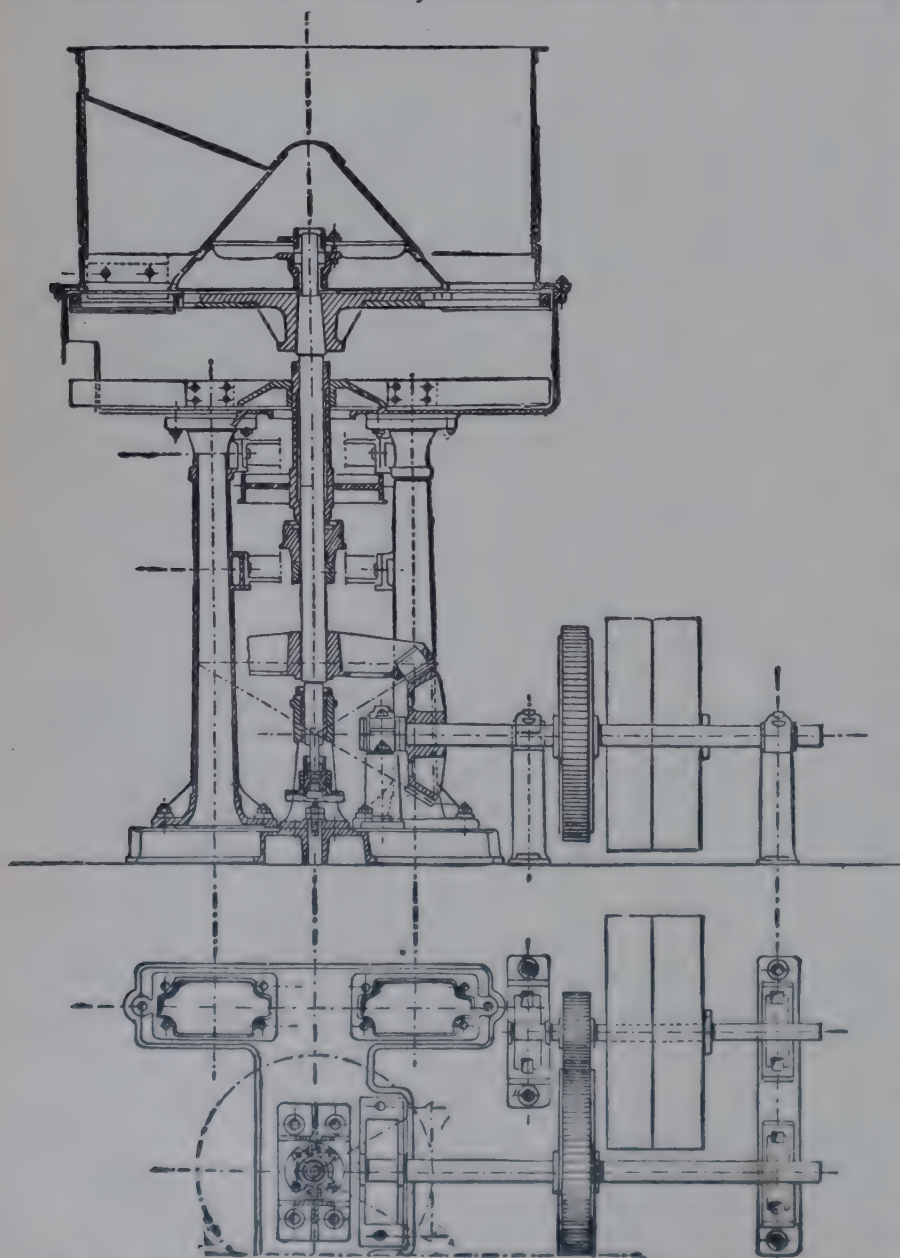


FIG. 51a.—Beet Slicing Machine. (Brand & Lhuillier, Brünn.)



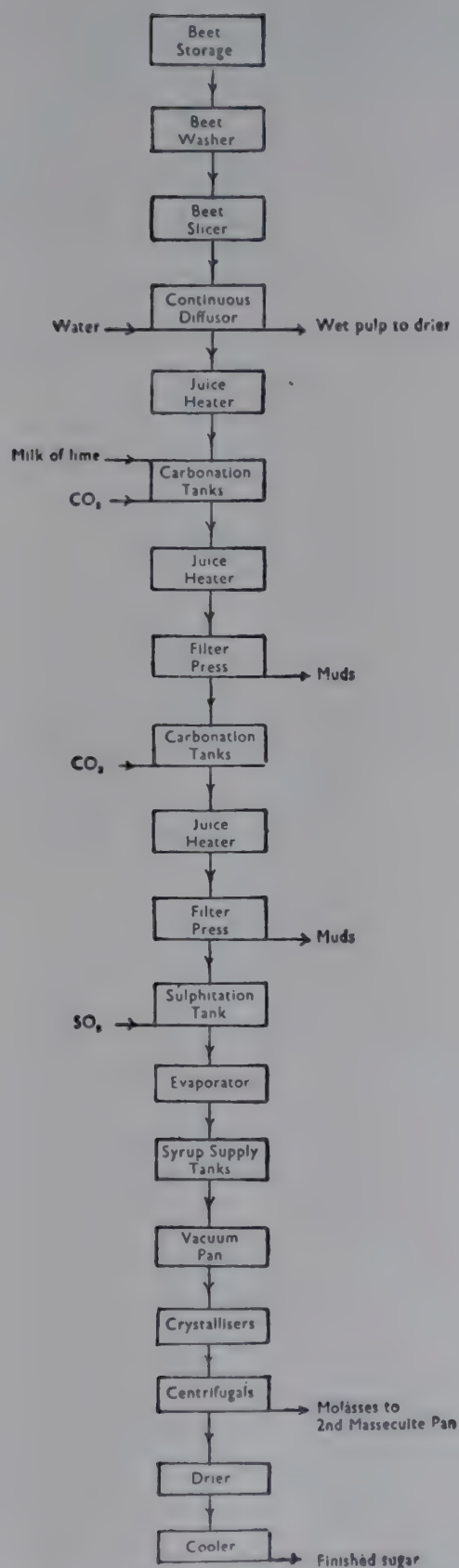


FIG. 51b.—Flow Sheet of Beet Sugar Factory.

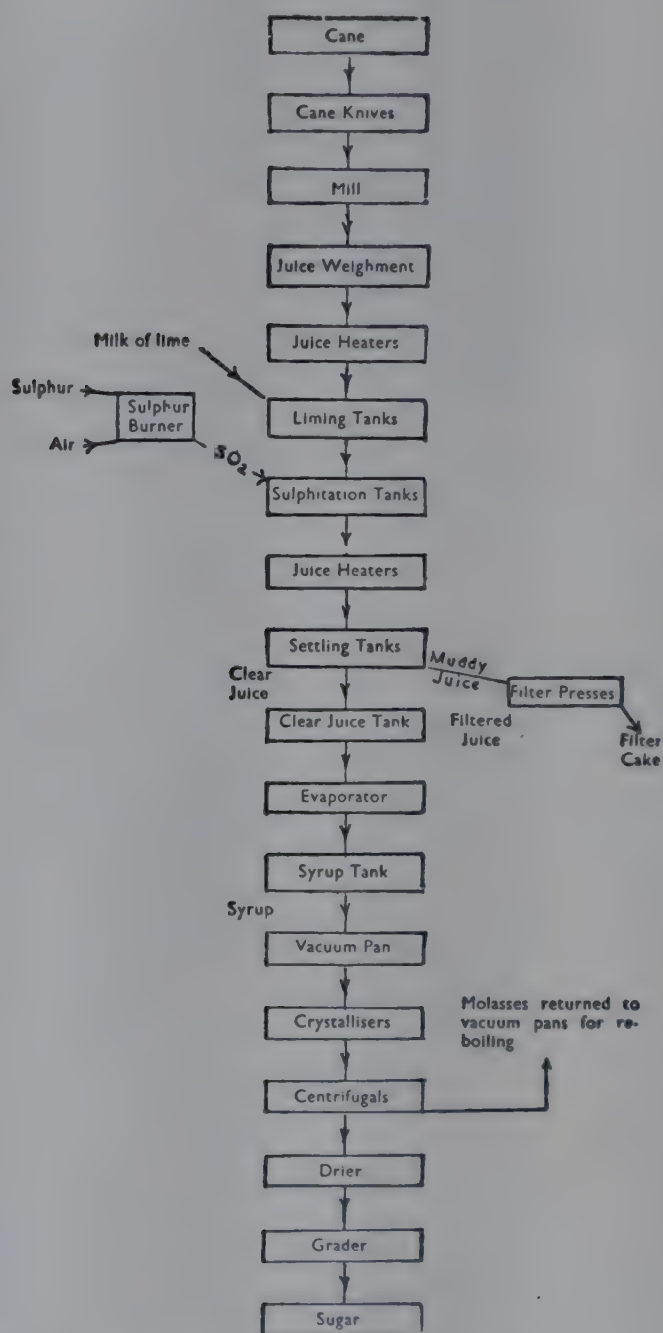


FIG. 51c.—Flow Sheet of Cane Sugar, etc., Factory.



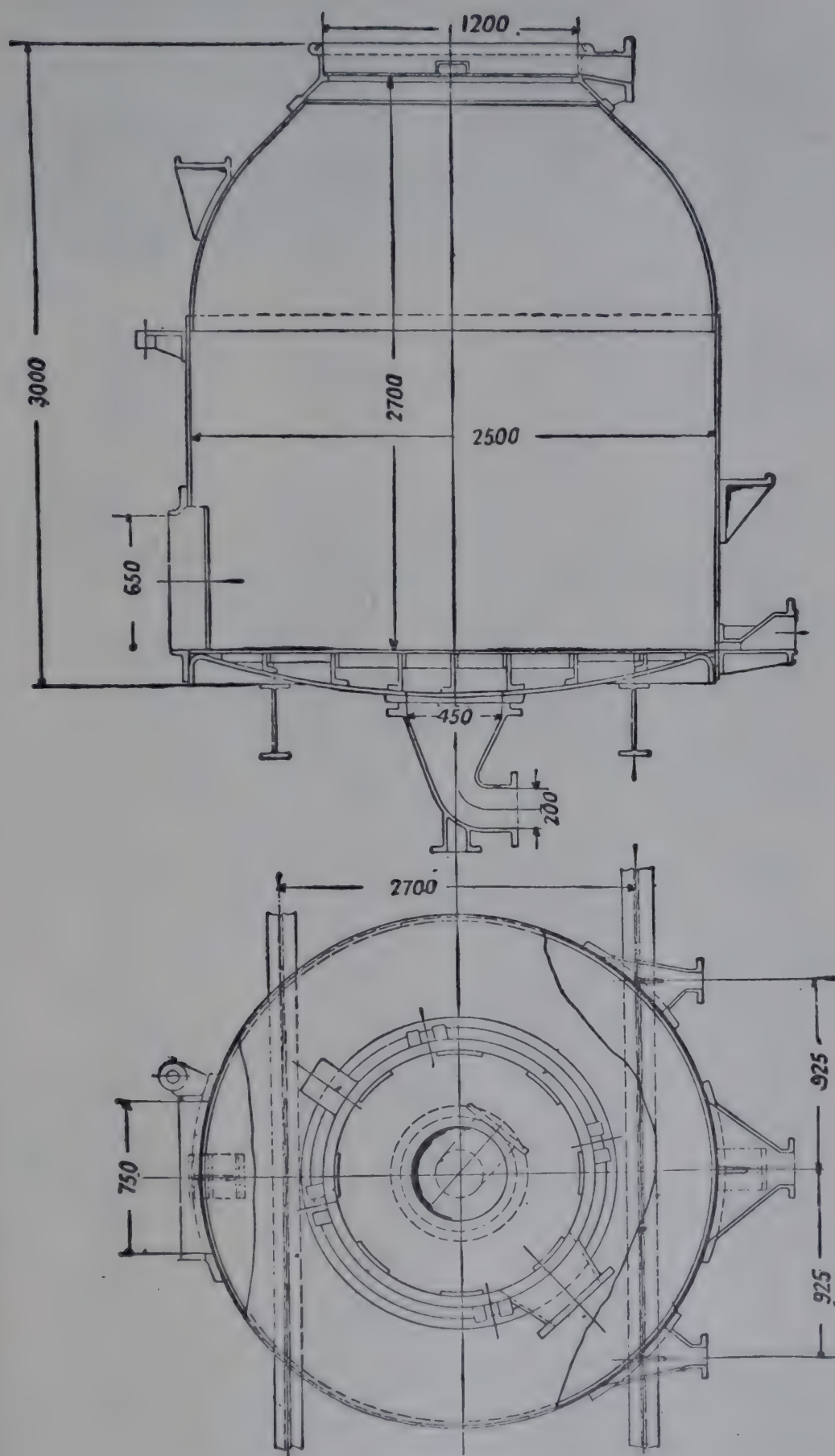


FIG. 52.—Diffuser of 115 Hectolitres Capacity. (Brand & Lhuillier, Brünn.)

sucrose, salts, and the simpler organic acids and amino-acids are permeable, whilst pectins and proteins are retained in the cell. Such small quantities of these latter as are found in the diffusates are derived from cells which have been cut or torn in slicing. The thin syrup of diffusion is therefore purer than the plant juice. Further, diffusion may be made exhaustive and economical by allowing the water from partially exhausted slices to pass on successively to fresh ones, thus ensuring the continuity of the operation and the production of diffusion juice in the ratio of not more than 115 to 100 of cell sap, which shall contain practically all the sugar. Or manifestly, if desired, any percentage of sugar may be left in the slices as is done in the Steffen process, where about 3 per cent. of sugar is not extracted.

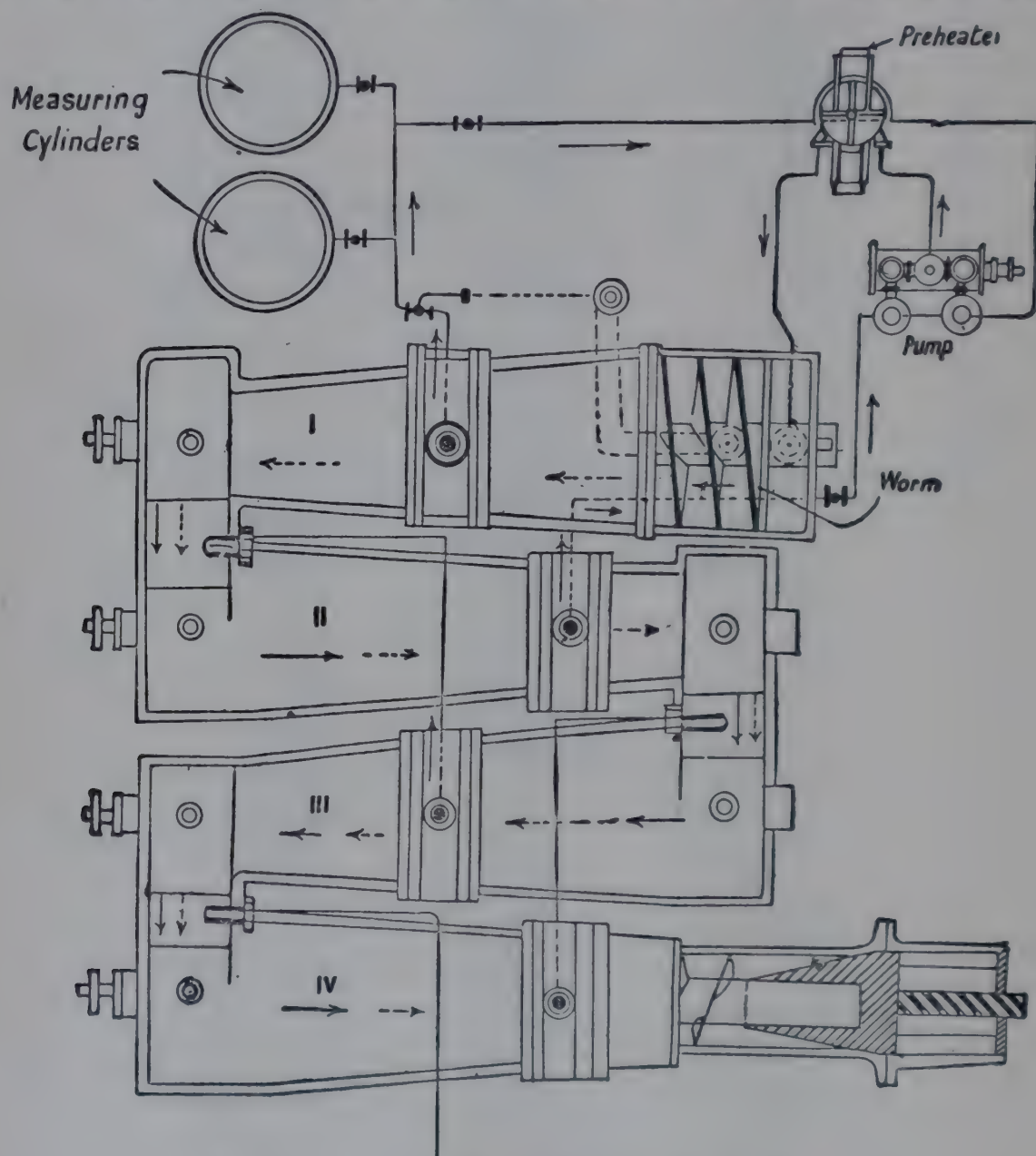


FIG. 53.— Pressure-Diffusion Process of Hyross-Rak.

A diffusion battery consists of several cells or diffusers arranged either in rows or in a circle, the number of cells varying from eight, but in modern work usually being from fourteen to sixteen. The diffusers are cylindrical iron vessels of from 4,000 to 8,000 litres capacity, and having on the average the ratio 1 : 1.3 of diameter to height, provided with manholes at the top for feeding, and having discharging doors either in the base or at the side. Calorisators may be interposed between the cells, or heating may be effected by steam injection.

The temperature for diffusion is from 70°–80° C. which should not be exceeded. The higher temperatures are better for sound beets and rapid work.

The lowest theoretical volume of diffusion juice is 94–95 per cent., that is, the sap content of the roots. In practice 105–106 per cent. calculated on the roots is usual. Higher dilution may mean more thorough extraction, but this may be commercially nullified by the greater fuel



consumption required for evaporation. From 0.15–0.35 per cent. approximately of residual sugar in the slices represents the limit of extraction.

In the working of a battery, that diffuser which has been freshly filled is charged with warm, nearly concentrated, juice, which can take up a little more sugar, and then with juices of diminishing strength down finally to fresh water, which passes on through successive diffusers to saturation. The last charge of water is usually admitted from below in order to loosen the mass of slices so as to facilitate the discharge of the exhausted slices, which are expelled by compressed air or water. The first cell of the series (*i.e.*, the one freshly filled) is charged under pressure, which serves to propel the juice from cell to cell of the battery. The time occupied for a battery of sixteen diffusers will be about six minutes for each cell, or ninety minutes for the battery.

In modern work certain variations in practical respects are in vogue. Hot diffusion systems (Malichar-Cerny, Naudet, and Kohler) have for their object the formation of more concentrated

juices by working rapidly at 85°, and further, by reason of albumen coagulation, the production of purer thin syrup. Saving in fuel and lime is thus effected.

In Kaiser's process the fresh slices are warmed by spent steam to about 70° before washing with juice.

The pressure-diffusion processes of Hyross-Rak and Steffen aim at the utilisation of the diffusion waste water, and the preparation of a more or less sugary diffusion slice for use as a cattle food.

Obviously such extraction methods must be combined with the installation of slice-drying plant.

In Hyross-Rak's process (Fig. 53) the slices are forced by an Archimedean screw through several diffusers arranged laterally. In the first, fresh slices are in contact with more concentrated juice and from this unit the thin syrup is withdrawn. In following units the successively poorer slices are in contact with thinner juices. The cells are cylindrical at the beginning, conical thereafter, and open into enlarged spaces from which an ingenious propeller transfers the slices to the wide end of the next cell. In spite of the 180° turn of the moving mass it is claimed that the process is quite continuous. The water consumption is given as 25–30 litres per 100 kilos of slices, the residue having 22 per cent. dry matter of 2.6–3.9 per cent. sugar content. Roots of 16.5–16.7 per cent. sugar gave juice of sp. gr. 1.0742, having 88.5–89.5 purity.

In Steffen's process the roots

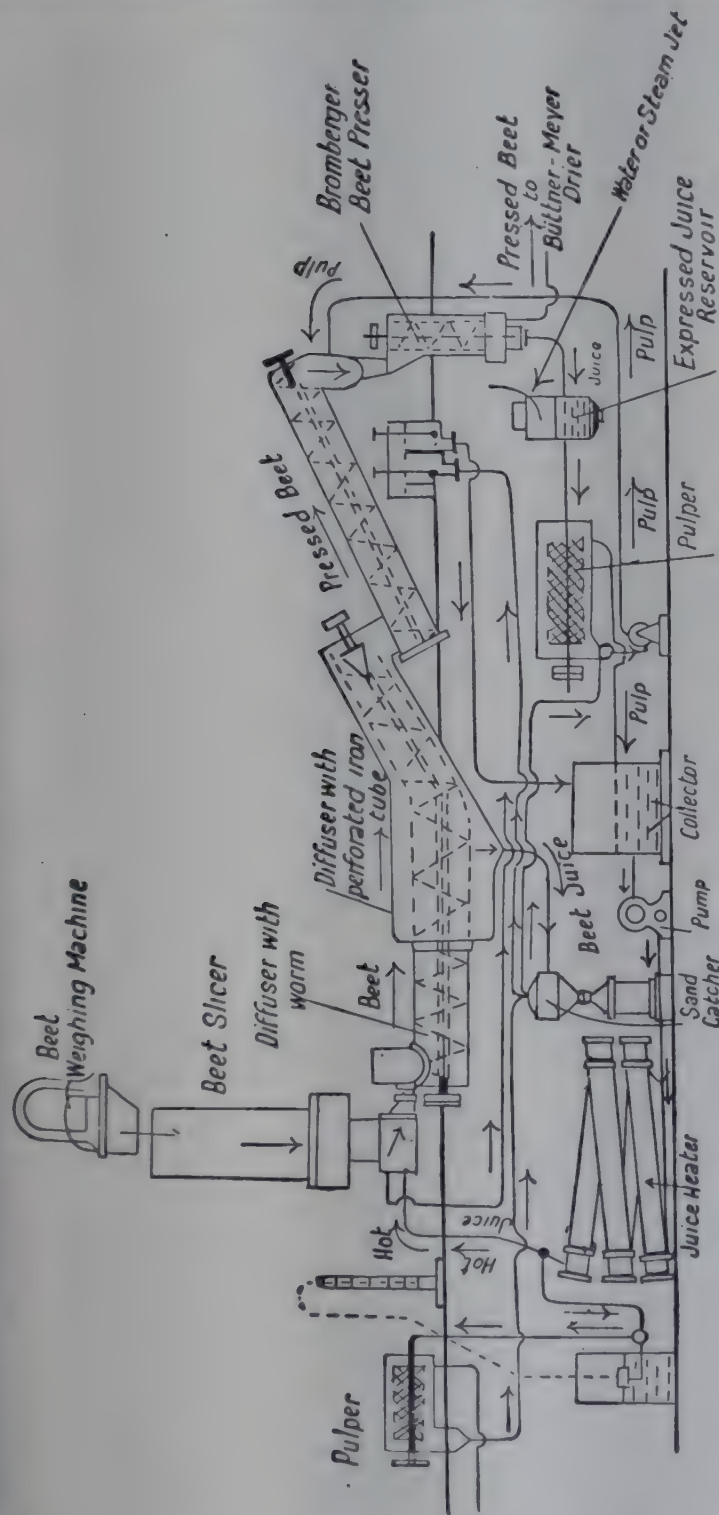


FIG. 54.—Pressure-Diffusion Process of Steffen.

a slicer, where slices of 1.5 mm. thickness are cut (Fig. 54). From the slicer they are carried through an inclined tube by hot syrup at 92°–97° into the diffuser consisting of a horizontal tube, in which the slices are at 82°–85°, leading to a second tube of perforated iron where separation of juice from slices takes place. The third element is an inclined tube, also perforated and built with the second into the same juice chamber. In it the slices are lifted from the syrup and at



the upper end submitted to preliminary pressure. Thence the slicers pass to a final inclined tube where mashing takes place and pass on to slice presses. The slices remain three minutes in the brew vessels and the whole interval up to completed pressing is about ten minutes.

In recent years several continuous methods have been adopted and installed in British beet sugar factories. Two well-known diffusers of this type are the "Rapid System" and the "Berge Type."\*

In the "Rapid System" (see Fig. 55) a cylindrical drum with a slight incline, approximately 75 ft. in length and 6 ft. diameter, is fitted with divisions. Blades are fitted to a shaft which runs the entire length of the drum, these blades lifting the cossettes or slices from one compartment to the next. The cossettes are preheated by steam, and meet a stream of water, heated to from 70° C. to 80° C., running down the incline. Thus the almost exhausted slices meet fresh water, and the incoming slices are in contact with the thick juice.

**Diffusion slices, or pulp,** result in the proportion of about 85 per cent. of the original roots. Undried slices contain on the average 6 per cent. of total solids and 94 per cent. water. About 0.2 per cent. of sugar remains in the pulp, excepting in the Steffen or similar processes when about 3 per cent. remains.

By pressing, the total solids may be raised from 6 to 10 or 15 per cent., *i.e.*, the yield of pulp may be reduced from 85 to 51 or 34 per cent. respectively. But strong pressure involves some loss of nutrient substance and pulp, and will therefore only be employed when it is intended to dry the pulp, in which case the saving of fuel will compensate the loss in question.

Pulp presses for the most part consist of Archimedean screws on perforated axes working within conical perforated cylinders. As the pulp is driven forward it is compressed, the water draining away by the perforations in the axis and wall of the cone. An installation may be made in which the pulp elevators end in conical press cylinders.

It is to be remarked that those processes in which the diffusion press water is returned to the batteries as above mentioned effect saving both of sugar and other nutrient substances, as well as solving the problem of waste water disposal.

Wet slices are often fed direct to farm stock, or are "siloe," that is, stacked in large heaps, when fermentation sets in with production of acidity due chiefly to lactic acid, and a fall in protein occurs. Wet slices do not, however, possess very great durability or commercial value, and in very many modern Continental works drying plant has been installed. Two systems are operated, namely, fire drying by furnace gases according to Büttner-Meyer, and steam drying according to Sperber, the former being more usual.

The composition of dried slices varies; the subjoined figures from Stift-Gredinger, "Zuckerrübenbau," illustrate this point.

	Ordinary Slices.		Steffen Sugar Slices.*	Hyross-Rak (Steam-Dried).†
	Fire-Dried.	Steam-Dried.		
Water . . . . .	4.19-15.80	8.36-11.76	6.05-13.0	2.79
Protein . . . . .	4.50-8.81	6.69-10.25	} 5.80-7.0 {	7.56
Amides . . . . .	0.06-1.31	0.12-0.25		0.88
Fat . . . . .	0.22-1.80	0.51-1.15	0.30-0.50	0.23
Carbohydrate . . . . .	47.70-62.73	55.14-60.64	66.50-69.10	61.45
Fibre . . . . .	13.60-22.84	18.45-21.60	10.50-19.95	21.76
Pure ash . . . . .	2.63-5.96	3.18-4.97	} 3.50-5.0 {	2.82
Sand . . . . .	0.02-2.94	0.04-1.13		2.51

In the Büttner-Meyer system the wet slices are fed into an oven, built into which are three tiers of horizontal rotating shafts having blades by means of which the slices are turned and propelled forward from set to set of agitators. In the opposite direction to that of the slice passes a current of mixed furnace gases and air, entering the kiln at 800°-1,000° C. By this

\* The description and working of this diffuser is fully described in *The International Sugar Journal* (1934), p. 473.

† Containing 30.0-38.4 per cent. sugar.

‡ Containing 12.6 per cent. sugar.



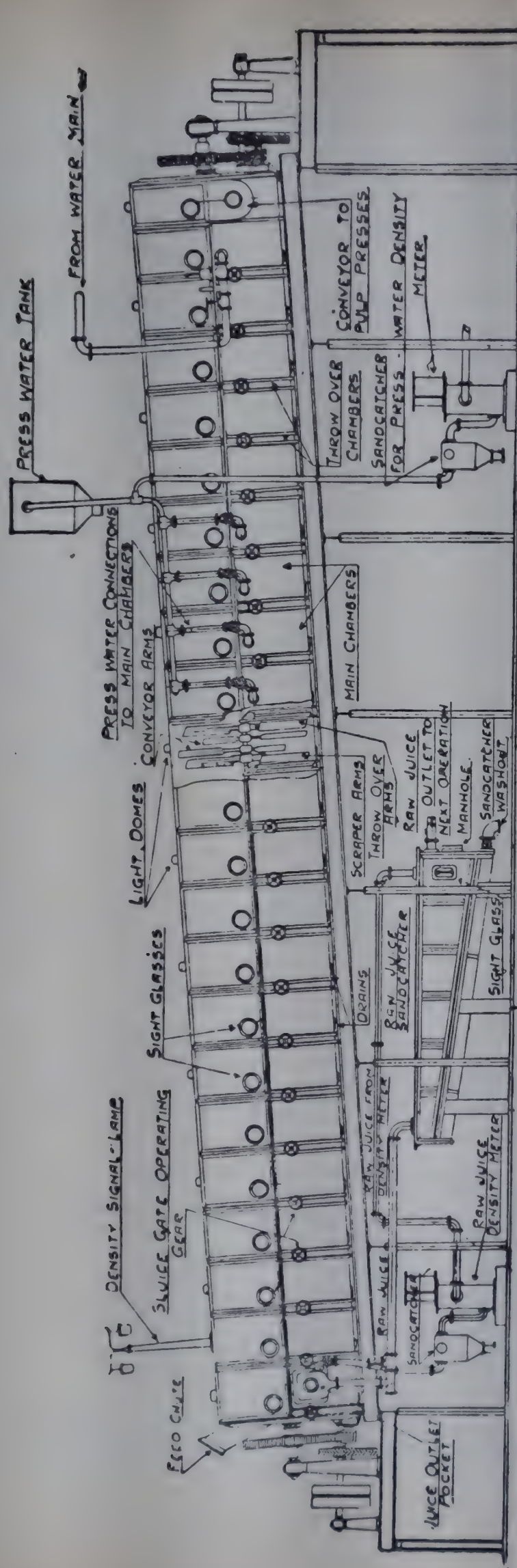


FIG. 55.—Continuous Diffuser “Rapid System.”

[Courtesy of Messrs Duncan Stewart & Co. Ltd.]

hot current the slices are rapidly dried, and by reason of evaporation do not probably go above  $100^{\circ}\text{C}$ . Drying is not, however, pressed too far in case of fire.

In steam-drying according to the **Sperber method**, the slices after wet pressing are ground—to facilitate drying—and fed into an iron chamber having four double-walled iron troughs, heated by spent steam. Each trough is provided with a pipe calorisor heated by live steam at 4–5 atmospheres, and with transport blades. The divided mass is thus passed along the first trough, on to the second, third, and fourth, alternating in direction. The disengaged steam is withdrawn by an exhaust, which also draws in warm air, a partial vacuum being produced, which aids drying.

**3. Purification of the Thin Syrup.**—Diffusion juice averages 11–15 per cent. sugar, and  $13^{\circ}$ – $17^{\circ}$  Balling, showing purity of 85.5–89.66, invert sugar not exceeding about 1 per cent., and ash being about 2.5–3.5 per cent.

Vegetable detritus from the batteries must be removed, and this is done by pulp filters, which are cylindrical fine sieves, in a wider containing cylinder. The juice, in passing through the filter, leaves solid particles on the sieve, which must be cleaned from time to time.

All practical systems of purification depend on the use of lime, which has been practised for many years. In simple “defecation,” after admixture with milk of lime and heating, the scum is removed. The great difficulty is in mixing the correct quantities. An excess of lime is prejudicial, since it acts on the reducing sugars; moreover, loss may occur through formation of the insoluble tribasic calcium sucate. These irregularities are entirely overcome by “carbonation,” which is universally employed in the beet industry. The general principle of carbonation is the treatment of the warm juice with milk of lime and precipitation of carbonate therefrom with carbon dioxide. Any insoluble sucate is thus decomposed, and the voluminous precipitated chalk carries down with it proteins and pectins, probably by absorption. This effect is similar to that of lime in the clarification of sewages, and the removal of colloid impurities is possibly a physical and not a chemical reaction. Most of the organic acids, notably oxalic, are also precipitated as lime salts.

Carbonation brings about a remarkable improvement in the mobility and colour of the juice, which becomes quite clear and limpid.

Before treatment with lime the juice is warmed. On leaving the diffusers it has a temperature of  $20^{\circ}$ – $35^{\circ}\text{C}$ ., and before liming it is raised to about  $80^{\circ}$ – $85^{\circ}\text{C}$ . with the object of coagulating some of the protein, which is thus rendered less liable to decomposition by the alkali. Sometimes the albumen is filtered through cloth, but this does not seem to be of special advantage.

Liming is performed either by means of milk of lime or by the immersion of lumps of quicklime.

In the “wet process” by milk of lime the warm juice is run into cylinders or “malaxeurs,” holding from two to three times the volume of juice from one diffuser, having an iron stirrer making ten to fifteen revolutions a minute. From above the calculated quantity, either measured or weighed, of cream of lime is added.

Special measuring vessels are used in which the weight of  $\text{CaO}$  delivered is shown on a graduated scale by pointers worked by floats in the cream of lime. On the average the addition of lime is in the proportion for 100 of roots for the first saturation of 2.5–3 per cent.  $\text{CaO}$ , and for the second saturation 0.25–0.5 per cent.  $\text{CaO}$ .

The quantity of milk of lime to be added and the volume change of juice resulting are to be exactly calculated. For instance, supposing it is desired to add 3 per cent. of lime to a juice of 115 per cent., and that the milk of lime has  $20^{\circ}$  Beaumé, a gravity corresponding to 206 g.  $\text{CaO}$  per litre; we have 3 kilos lime (to the 100 kilos roots) in 3,000:  $206 = 14.56$  litres milk of lime, weighing  $14.56 \times 1.162 = 16.92$  kilos. Or about 17 per cent. calculated on roots, or 12.66 per cent. by volume, calculated on dilution 115 per cent. Further, the dilution is  $16.92 - 3 = 13.92$  per cent. of water on roots or 12.1 per cent. on diffusion juice.

“Dry liming” must be effected by immersing the quicklime in a flat sieve in the juice which is kept actively circulating by stirrers. Otherwise considerable local superheating due to slaking will occur, with corresponding decomposition of the sugar solution.



with Turbine

Scale = 1:30

with Stirrers

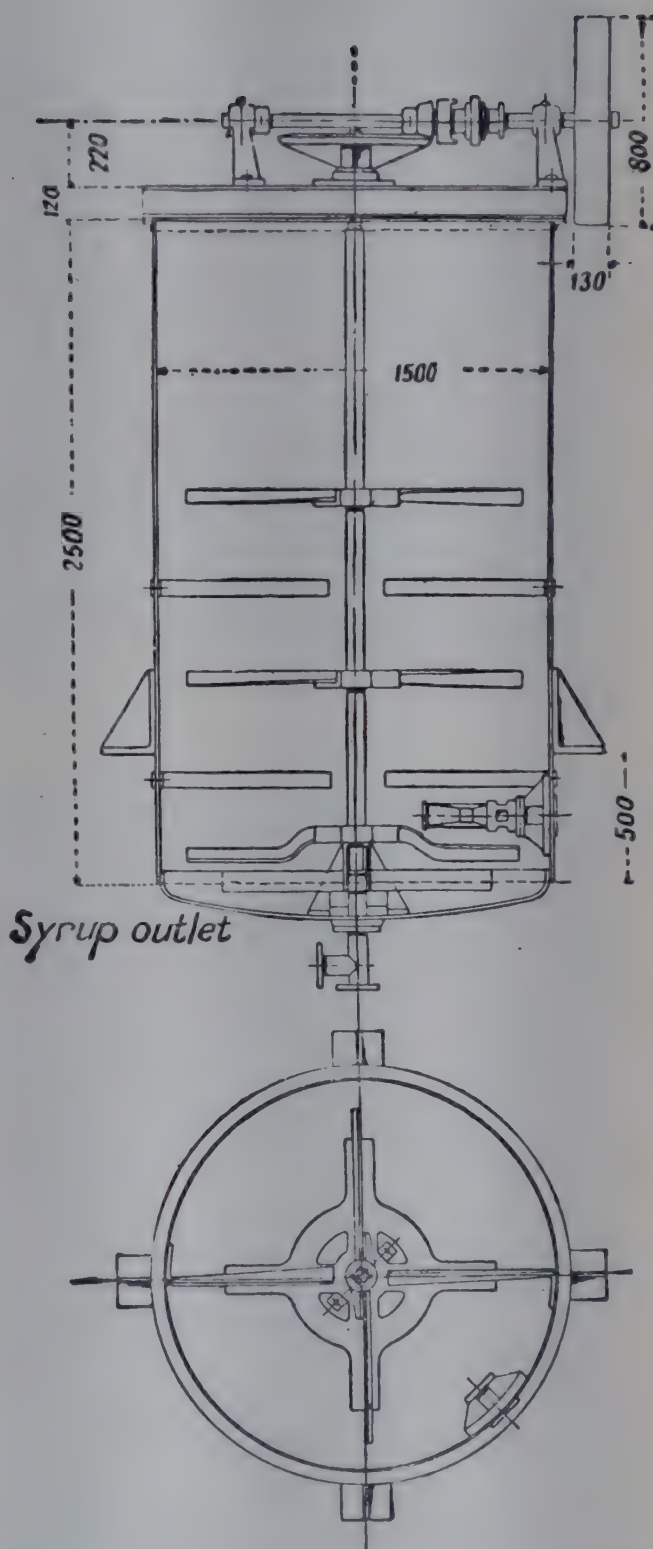
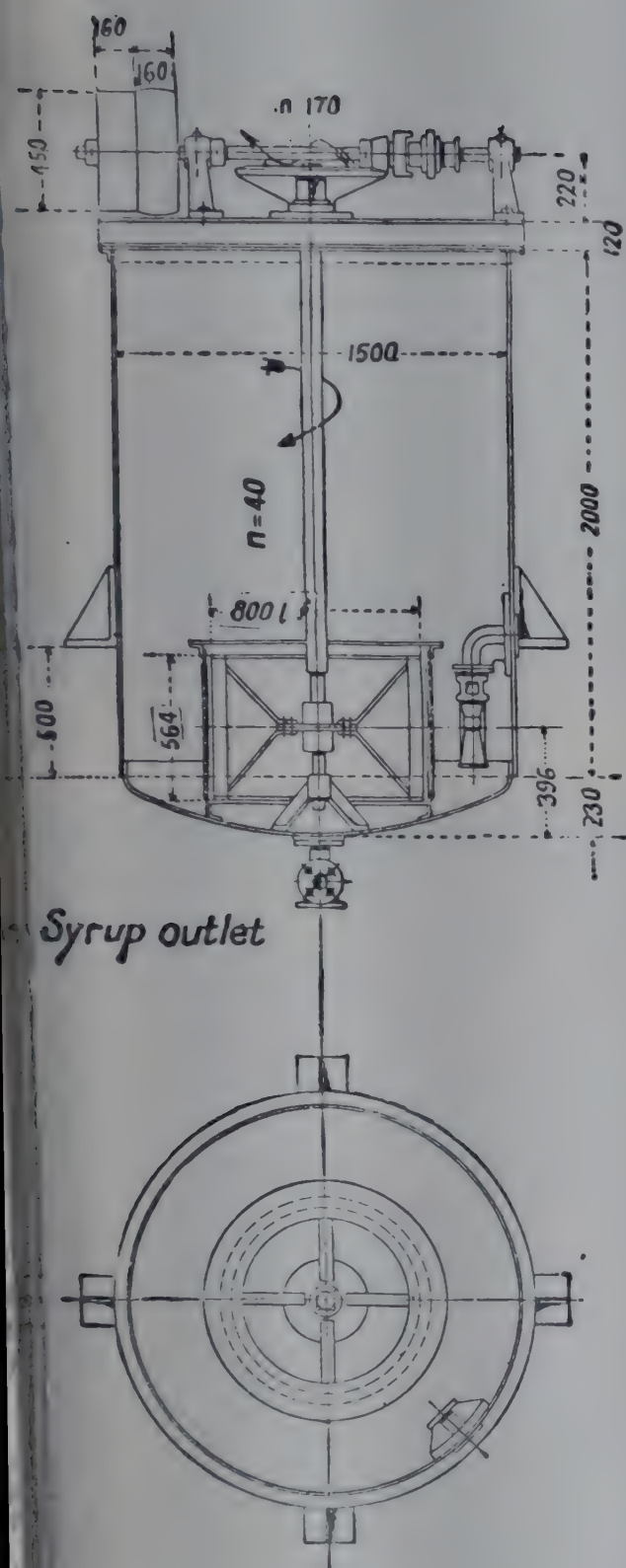


FIG. 56.—Saturators. (Brand &amp; Lhuillier, Brünn.)

Opinion varies as to the relative advantages of wet and dry liming. The solubility of quick-lime in sugar is greater than that of slaked lime on account of the readier formation of sucrares by the former agent, and it is claimed that clearer syrups are got therefrom. In dry liming dilution is avoided, but on the other hand in wet liming the liquor from the lime filter presses can be used for slaking, whereas in dry liming it has to be evaporated, so that this advantage is cancelled. For dry liming  $85^{\circ}$  of heating is desirable else the decomposition of amides is incomplete. In the event of invert sugar being present dry liming tends to its decomposition,

the products forming coloured iron salts. In neither process does the lime sludge from the filter presses contain notable quantities of sugar.

The juice having been limed passes to the "saturators," tall four-sided or cylindrical iron vessels, into which the carbon dioxide is pumped and injected into the liquid under pressure through various types of gas dividers (Fig. 56).

Only about one-third to one-half of the gas is absorbed, the remainder passing out of the saturator. Temperature is maintained by a copper steam coil. At first the juice foams greatly, and has a somewhat gelatinous consistency, being unfilterable. Foam is destroyed by the sparing introduction of oil (tallow or castor oil) or by blowing steam direct on to the surface. As saturation proceeds the current of gas is increased, and the precipitate shows greater tendency to settle.

When an alkalinity of 0.05–0.06 per cent. by phenolphthalein titration, and reckoned as CaO, is attained the first saturation is finished in from twelve to fifteen minutes.

Continuous carbonation is designed to secure more complete absorption of the gas. The current of gas is divided by means of a turbine, and distributed through the mass of juice in a saturator of the ordinary type, having at a height of about 2 metres an outlet conducting the liquid to a second similar tank. The gas and juice outlet valves being opened, the admission of juice is so regulated that it passes over into the second saturator with an alkalinity of about 0.14 per cent., and is then saturated further, so that a continuous stream of 0.05–0.06 per cent. CaO may leave the installation.

After passing through a sand and stone trap the turbid fluid is pumped to the filter presses. These are all based on the well-known Dehne frame-press system, p. 34.

Washing of the sludge cakes is necessary, the degree of washing being determined by considerations of fuel consumption involved in extra evaporation, and is seldom pushed to the limit. Unwashed sludge cake forms about 12 per cent. reckoned on the weight of roots, and contains about 60 per cent. of syrup, equivalent to 7–8 per cent. of sugar, thus meaning a loss if unwashed of about 1 per cent. of sugar reckoned on the roots.

The sludge cakes, which have manurial value, vary in composition according to figures quoted by Stift-Gredinger as shown:—

Water	-	-	-	30.08 to 59.31	Nitrogen	-	-	-	0.12 to 0.41
Chalk	-	-	-	28.6 „ 50.00	Phosphoric acid	-	-	-	0.50 „ 2.22
Lime	-	-	-	0.10 „ 1.51	Organic matter	-	-	-	7.11 „ 12.1
Potash	-	-	-	0.04 „ 0.40					

Second saturation follows the same course as the first, the preliminary heating being to about 90° C. and the liming being to the extent of 0.1–0.5 per cent. A third saturation is sometimes adopted, which may be done by carbon dioxide, or by sulphur dioxide, or a mixture of both. Sulphitation of the thin syrup effects decolourisation, and the traces of sulphite remaining in the juice act as a preservative, but are liable to form incrustations in the subsequent evaporation, so that generally sulphitation is applied to the thick syrup.

Lime burning is manifestly an integral part of sugar factory routine, yielding both the lime and carbon dioxide required. Details of this process are in this connection superfluous.

The preliminary treatment of cane for the extraction of juice and its clarification necessarily differs from that followed with beet partly on account of the different form and texture of the plant, and also from the fact that in most cane districts fuel is scarce, and the residual fibre, or "bagasse," forms the needful combustible.

Cane must be delivered as soon as possible to the mills, as inversion of sucrose is rapid in cut canes. Transportation is usually carried out by one of the following: rail cane cars, motor trucks with or without trailers, bullock carts, and canal barges. Great difficulty is experienced in loading and unloading cane, therefore the type of vehicle used is designed to facilitate easy handling at these points.



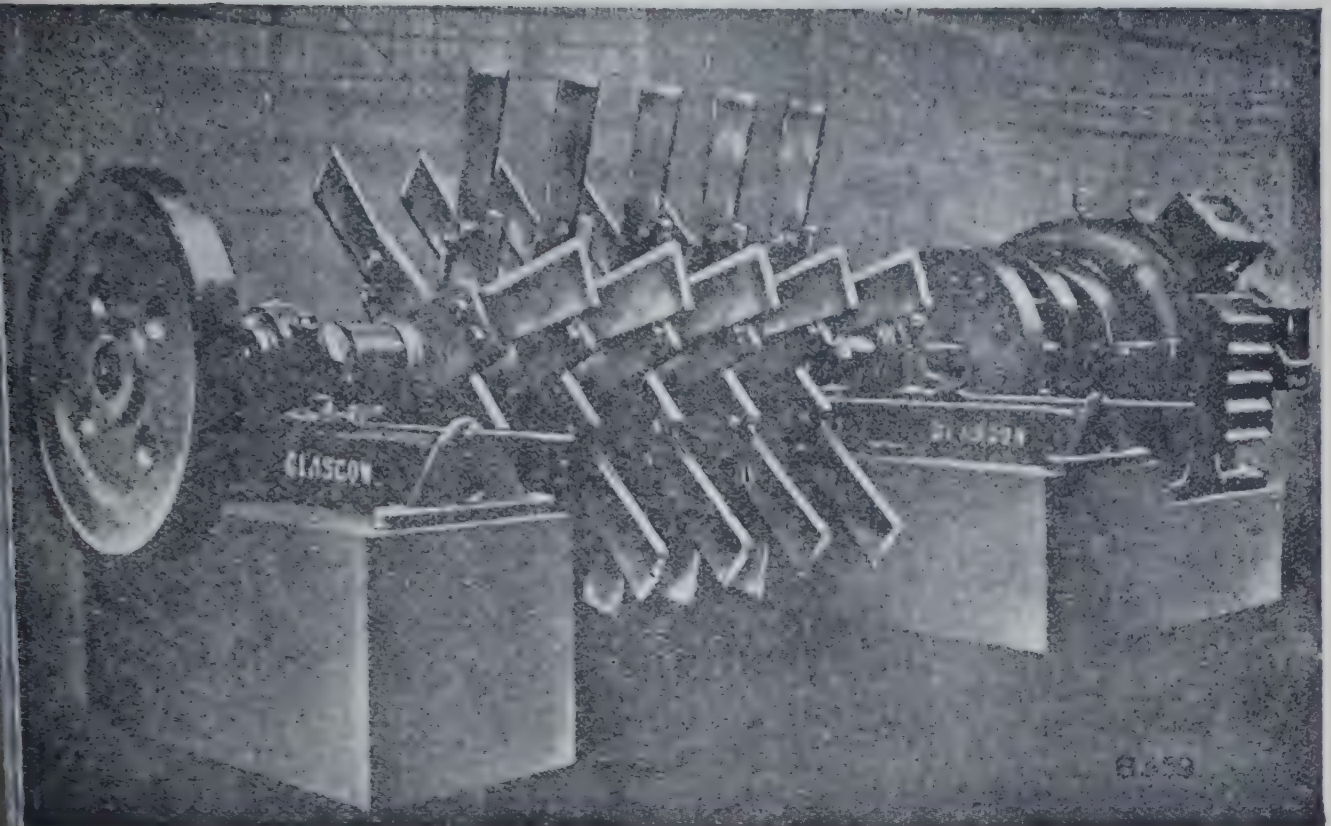


FIG. 56a.—Revolving Cane Knives.

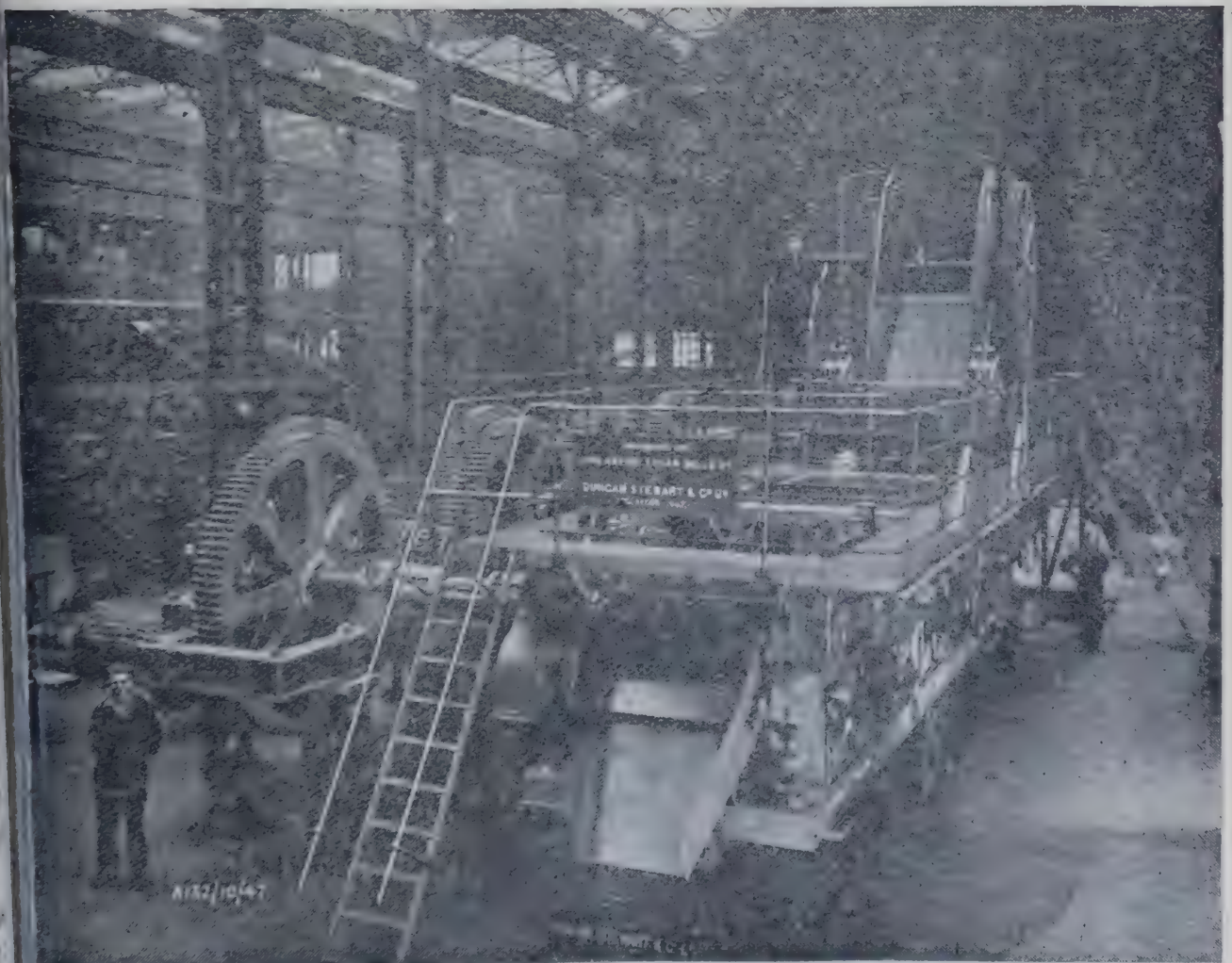


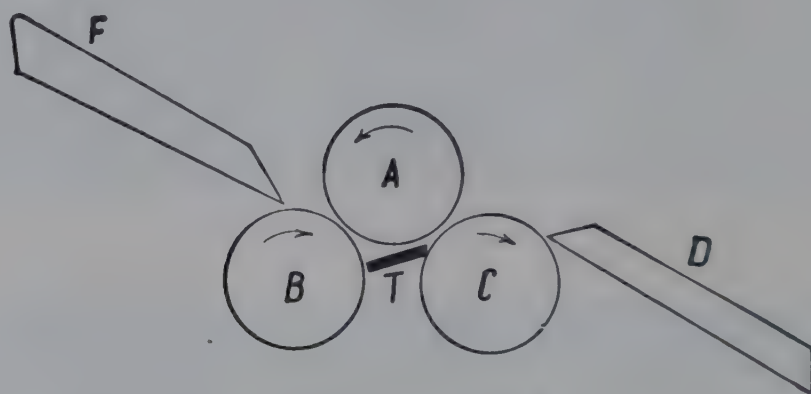
FIG. 56b.—Three Roller Cane Mill. Front View.



The cane is unloaded, as evenly as possible, on to a conveyor belt or "carrier" which traverses from the cane yard to the mill. Various mechanical methods are used in unloading the cane—derricks, raking devices, and hydraulic tipping devices which tip the entire rail truck into the carrier.

Before entering the mill, the cane is cut into chips during its passage on the carrier by passing it through rapidly revolving cane knives (see Fig. 56a). These knives are usually placed spirally on a shaft, about 2-in. spacing, the shaft being driven by an electric motor or steam engine to give a speed of about 500 r.p.m. A clearance of from 3 in. to 6 in. is usually allowed between the tip of the knives and the bottom of the carrier. The cane in the form of chips gives better extraction from the mills, and at the same time allows the cane to be evenly fed, giving also maximum capacity.

The modern mill tandem consists of four or more sets of three roller mills, following a two-roller crusher. The crusher rollers extract from 40 to 70 per cent. of the juice and are, along with the knives, responsible for the preparation of an even blanket of cane to the following mills. Rollers are of cast iron, with



SECTION OF CANE SUGAR CRUSHING ROLLS

FIG. 57.

an open grain, and are deeply grooved with various types of grooving to facilitate the tearing of the cane, with easy flow of the juice. Normally, mills are driven by steam engines through gearing, but electric driven mills are also in use. There is one mill still in operation which is water driven. The cane from the crusher rolls usually falls in an even blanket down a chute into the first of the three roller mills. Two are on one level and the third above, rotating as shown by the arrows in Fig. 57 (top).

Rollers are under pressure, either hydraulic or spring loaded, and some manufacturers also load the discharge roll.

The partly crushed canes are fed along F to the combination AB, or the feed roller, where they are crushed, and directed by the adjustable trash plate to the "bagasse," or discharge, roller, where expression of juice chiefly takes place. After expression the bagasse (cane with juice removed) passes along D, which is an intermediate carrier between the first and second mill.

These usually consist of three smooth rollers, two on one level and the third above, rotating as shown by the arrows (Fig. 57).

The canes are fed along F to the combination AB, or the feed roller, where they are crushed, and directed by the adjustable curved plate or "trash" T to the bagasse roller AC, where expression of juice chiefly takes place. The bagasse passes along D. Combinations of three-system rollers are in general use, often combined with a preliminary crusher of the Krajewski type, consisting of two rollers having V-shaped teeth whereby the work of the first mill is relieved.



It is obvious that no crushing can effect a complete expression of juice, and maceration of the crushed bagasse is resorted to. Upon leaving the rollers the compressed fibrous mass on expanding is able to take up water fairly thoroughly, although not so completely as to fill up all the cells. Maceration with the last mill juice of the bagasse leaving the first mill may be performed if the crushing is sufficiently powerful to disintegrate the cane. According to this method of working, the juice (in a three-mill system) from mills 1 and 2 passes to the clarifiers, that from 3 being returned to the bagasse leaving 1.

Maceration must not be carried too far, else the extra cost of evaporation will not be covered by the increase of sugar extracted. According to Prinsen Geerligs 12-16 per cent. maceration gives good results in Java, the sucrose content of bagasse being 4.5 per cent. Figures quoted by the same author of the results of a twelve-roller mill afford a good idea of the kind of results obtainable.

Sucrose in cane	-	-	-	15.37	Sucrose lost in bagasse on 100	
Fibre in cane	-	-	-	10.98	cane	- - - - 0.76
Sucrose in bagasse	-	-	-	3.28	Extraction on 100 sucrose in cane	95.40
Moisture in bagasse	-	-	-	45.66	Dilution by maceration on 100	
Fibre in bagasse	-	-	-	49.92	normal juice	- - - - 26.12

In consideration of the loss of sucrose, and further, of the expression of objectionable colloidal impurities, very naturally much attention has been directed to the practicability of diffusion for cane extraction, but diffusion is not applicable in practice for several reasons. Although the juice contains less impurity, diffusion in test experiments quoted by Geerligs gave a 95 per cent. extraction, with a 25 per cent. dilution, or only 2 per cent. more than crushing with a 14 per cent. dilution. But the chief difficulty seems to be in respect to the bagasse, which from diffusion is saturated and must therefore be either sun dried or rolled before use as fuel, whilst, having a finer texture, its value as fuel is impaired. Greater work is thrown on the boilers for the extra evaporation and driving of the very powerful slicers needed to prepare the cane for diffusion.

Crushing with subsequent systematic lixiviation of the bagasse, according to Perrichon, has been successfully practised in Egypt. The bagasse is fed into waggons having sieve false bottoms and discharge valves, and holding about  $1\frac{3}{4}$  tons of bagasse. Hot water is run on to the contents of the waggon, and after about seven minutes drawn off and pumped up to a tank above the waggon levels, whence after reheating it passes to a second waggon, and so on over nine waggons. This system gives probably about 15 per cent. dilution, and accomplishes an extraction equivalent to 96.7 per cent. on juice.

In the Naudet process the bagasse from a double mill is charged into a diffuser in which it is mixed with cold mill juice. The juice is drawn off by a centrifugal pump, passed through a heater and liming trough, returned to the top of the diffuser, and then percolates the bagasse. In this way defecation is effected. The bagasse is afterwards exhausted systematically as in ordinary diffusion. The juice having parted with its impurities to the bagasse is ready for evaporation.

The Harvey firm have installed Naudet plants, and Mr Harvey \* reports that an extraction of 95 per cent. has been obtained in Madeira, whilst in Porto Rico 96 per cent. sucrose was recovered with a 9 per cent. dilution in 100 of cane (equal to about 10 per cent. in 100 of juice), the syrup having 1.3° Brix [total solid] less than dry milled juice, and the same quotient of purity.

The **composition of cane juice** varies. The following figures extracted from Prinsen Geerligs' "Cane Sugar" will serve to give an idea as to its components. It will be observed that reducing or invert sugar is the constituent which mainly distinguishes cane from beet juice.

The figures display in a clear fashion how glucose, being more diffusible, is expressed more in the first mill, whereas the colloidal pectins and albumens are expressed more completely in the second and third. As regards the maceration juices, these, if reduced by calculation to original gravity, show similar compositions to those got by expression without maceration.

\* *International Sugar Journal*, 1905, 326.



	Black Java Cane without Maceration.			Borneo Cane with Maceration.		
	First Mill.	Second Mill.	Third Mill.	First Mill.	Second Mill. Diluted Juice.	Third Mill. Diluted Juice.
* Brix - - -	19.2	19.3	19.0	18.5	14.8	6.7
Sucrose - - -	16.49	16.33	15.95	16.76	12.65	5.50
Reducing sugar -	1.98	1.57	1.52	0.89	0.59	0.33
Ash - - -	0.28	0.41	0.42	0.244	0.425	0.199
Gum and pectin -	0.125	0.376	1.250	0.063	0.150	0.099
Albumen - - -	0.025	0.092	0.054	0.024	0.068	0.047
Free acid - - -	0.048	0.072	0.096	0.042	0.039	0.016
Quotient of purity*	85.9	84.4	84.0	90.59	85.47	82.10
Glucose ratio† -	12.0	9.6	9.5	5.3	4.7	6.0

The clarification of cane juice is still largely performed by the old style process of defecation with lime for the production of brown or raw sugar. Raw sugar is manufactured to a purity which gives a polarisation of  $96.5^{\circ}$  to  $97^{\circ}$ , and is usually subsequently sent to the refineries for further purification. An off-white or plantation white sugar is manufactured in Java, India, and other parts, using the sulphitation or carbonation processes. Frequently, sugar produced from especially the latter process is of very high quality.

In the manufacture of raw sugar, the juice from the crusher rolls and the first and second mills is pumped to juice weighment vessels, where it is weighed and samples taken. This is for calculation of the quantity of sugar entering the process. On leaving the scales milk of lime is added and mixed, often in a receiving tank under the scales, until the pH of the juice is from 8.0 to 8.4. The actual pH decided upon varies with the nature of the juice and is a question to be decided by preliminary experiment. In some cases the juice is limed as it leaves the mill by an automatic lining device. When the lime is thoroughly mixed the juice is pumped through juice heaters or heat exchangers to bring it to the boil. These juice heaters are closed tubular vessels, the juice passing through the inside of brass tubes, the outside of the tubes being heated with exhaust steam at 10–15 lbs. per sq. in., from the prime movers.

The juice from the juice heaters is run into settling tanks or some type of continuous clarifier. An ordinary settling tank is normally rectangular in shape, with an overflow gutter, an adjustable pipe for drawing off the clear juice, and a bottom discharge pipe for drawing off the muds. Juice on settling divides into three layers at the bottom, the muds which consist of a flocculent precipitate of calcium phosphate and other insoluble salts, which carry down the coarse suspended matter, adsorbing some of the colloids and occluding the finer suspension. In the centre is the clear juice, and on top a scum, consisting mainly of fine fibre from the cane, commonly known as bagacillo. This latter is first brushed off the top into the gutter, and the adjustable pipe lowered to a depth to run off the clear juice. As the level of the juice in the tank falls, it is necessary to make adjustments to the pipe to ensure the regular flow continues. When the juice shows signs of becoming cloudy the decantation is stopped, and the muddy precipitate is discharged from the bottom to a mud receiving tank.

There are various types of continuous settlers, the best known being the Dorr clarifier. The use of a continuous settler has many advantages—less labour, less heat losses, greater concentration of muds, with consequent reduction of losses of sucrose in the muds, and better clarification.

The Dorr clarifier consists of a circular tank with a conical bottom and a parallel conical top. The interior is divided into a series of shallow compartments

\* Percentage sugar in total solids.

† Glucose per 100 parts sucrose.



which are conical and parallel to the top and bottom. There is a central opening through the cover and trays to the bottom, which acts as a mud passage, common to all the trays. On the top of the tank is a small tank known as a "feedwell."

An electric motor is fixed above the tank and supplies power for the "mud thickness," and a diaphragm pump which withdraws the mud. A central shaft passes down the tank to the bottom, and keyed to the shaft, just above the bottom, and bottom of each tray, are spiders, the four branches supporting steel arms, extending to the periphery of the tank. Small scraper plates of brass are carried by the steel arms, and these scrapers rest lightly on the trays and bottom. The brass plates are driven lightly round the trays, whilst in the feedwell, on the

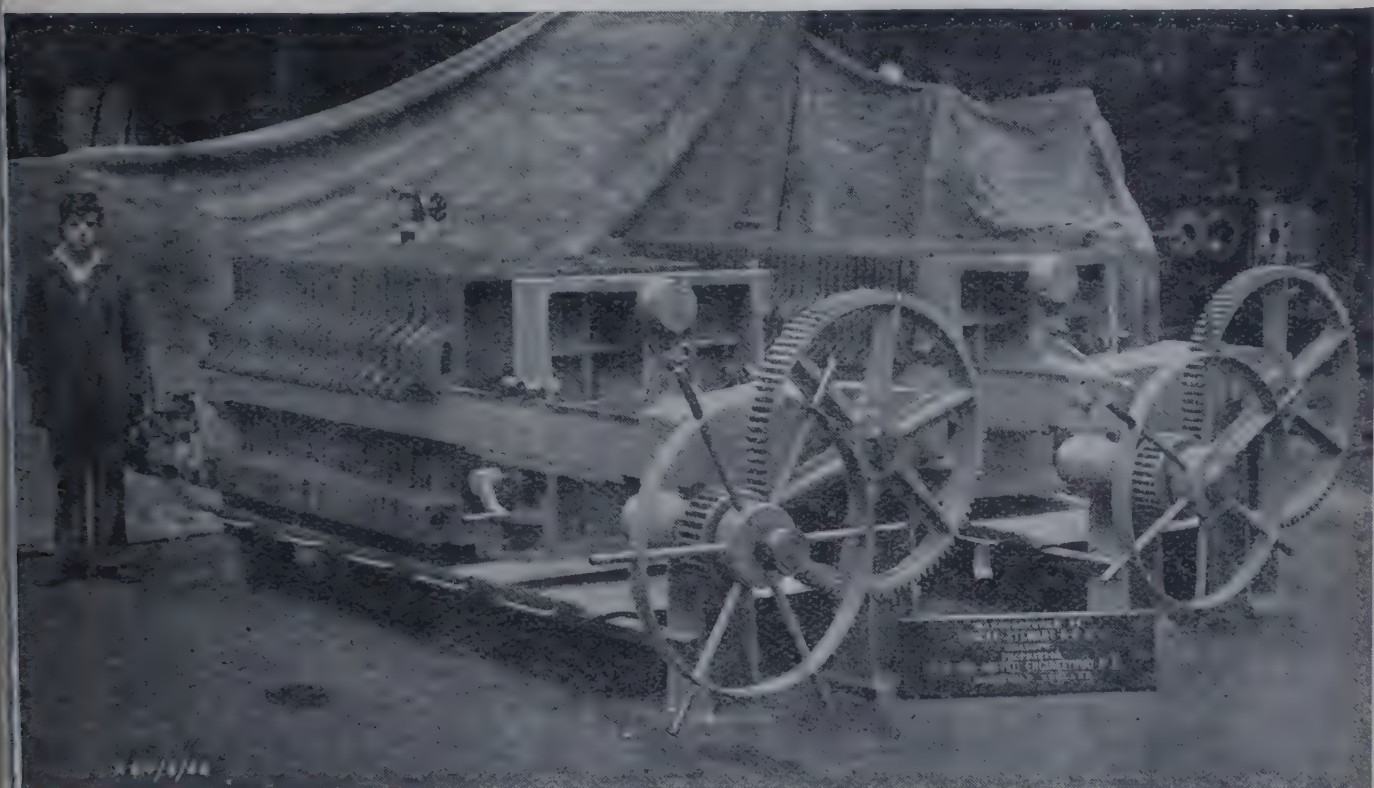


FIG. 58.—Filter Presses.

same main shaft, are four radial paddles for removing the foam into a discharge canal. Underneath the cover of the trays, at peripheral points, are the clear juice overflow pipes, which are connected to an overflow bin. Each outlet pipe is fitted with an adjustable sleeve to adjust the quantity of juice from each compartment. The difference in head between inlet and outlet provides the force to cause the juice to flow through the clarifier.

Continuous operation is thus obtained. Hot limed juice enters the feedwell, the foam rises and is removed by the four paddles, the heavy solids settle through the central opening, the bagacillo travels to the periphery and is carried down with the muds, and the revolving arms push the mud down the central opening where it is withdrawn by the diaphragm pump.

The clear juice from both the ordinary settlers and the clarifier is transferred to a clear juice storage tank, whilst the muds are sent, as mentioned already, to the mud tank.

The muds are blown up with open steam and pumped through a filter press, the clear juice or press juice being returned to the clear juice storage tank, whilst the muds are washed with hot water, the excess water driven out by steam, and the washings either returned to the mill for macerating or sent direct to the clear juice tank. As the press cake is rich in organic matter and phosphates it is



usually returned to the fields as fertiliser, after it has been allowed to rot for a year. The rotting inverts and destroys any remaining sugars which would attract white ants. Many types of presses are used, normally the plate and frame press is used (see Fig. 58), but many factories are now changing over to the continuous filter presses which reduces the labour costs.

The only difference in the defecation process for raw sugar and the sulphitation process for plantation white sugar is in the addition of sulphur dioxide to the limed juice. The juice is limed slightly heavier, and the sulphur dioxide is

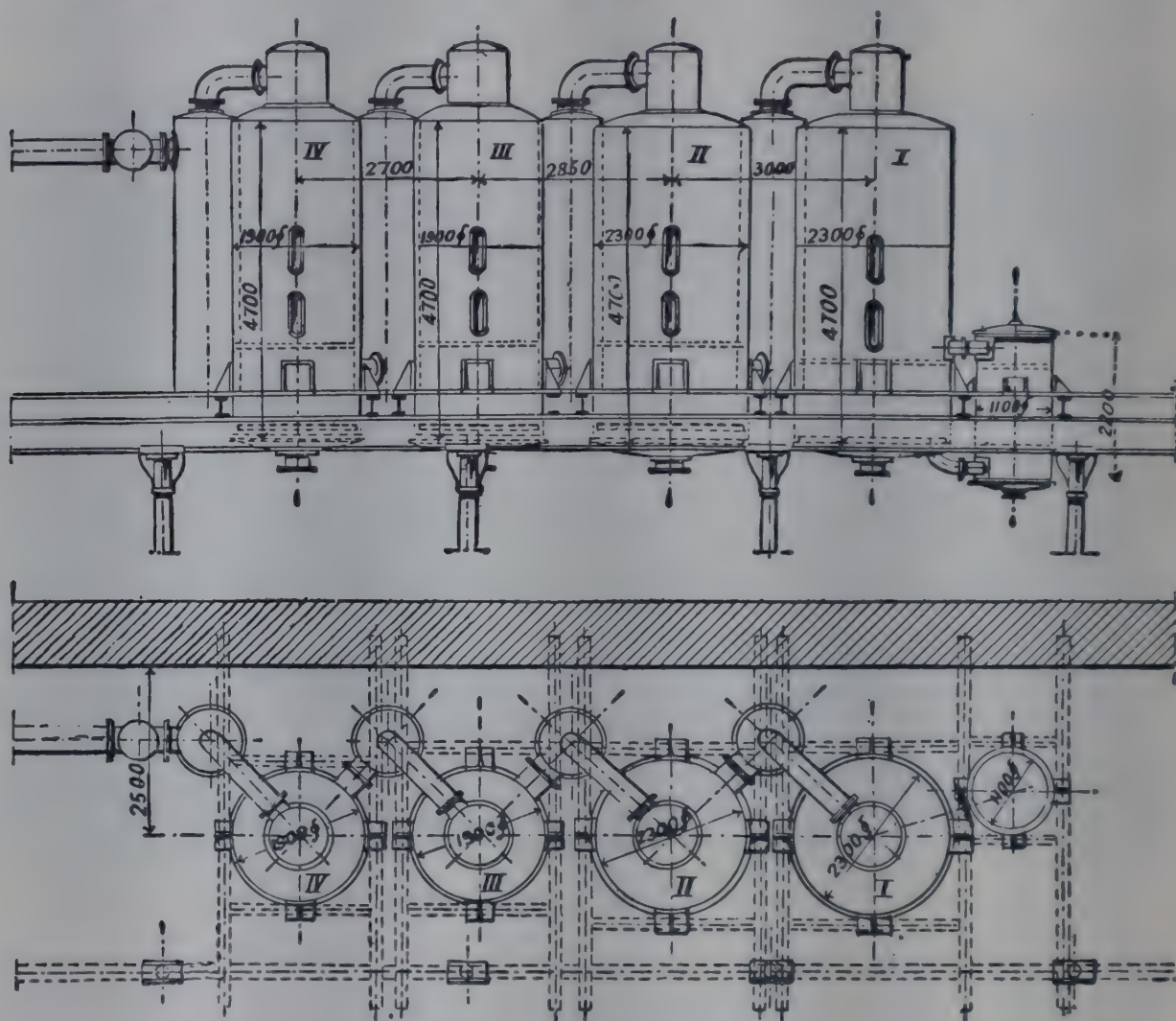


FIG. 59.—Quadruple-Effect Evaporators. (Brand & Lhuillier, Brünn.)

passed through the juice until a pH of 7.0 is obtained. More sulphur dioxide is usually passed into the thick juice or syrup at a later stage. The sugar produced in a sulphitation sugar factory is also more carefully freed from the film of molasses by double centrifuging. (See Flow Diagram of Sulphitation Process, Fig. 51b.)

The carbonation process for plantation white sugar from cane, is similar to that used in beet sugar factories. (See Flow Diagram for Carbonation Process, Fig. 51c.)

**Concentration to Thick Syrup.**—This used to be done in open pans over free fires, a process which tends to the formation of caramel and invert sugar, and which was most wasteful of fuel. Heating by means of steam coils was next adopted, a process ultimately supplanted by "multiple-effect" evaporation introduced by Rillieux and modified by Jelinek. In principle the process is simple. Steam from a closed juice evaporator is caused to heat a second at lower temperature, which in its turn heats a third in triple-effect working; or a fourth and



sometimes a fifth vessel may be added in quadruple and quintuple effect (Fig. 59). The last vessel is in connection with an exhaust pump, whereby steam is removed and pressure reduced, so that boiling takes place at a lower temperature, with the result that very little heat is lost. The syrup passes from the first vessel onward with increasing concentration, and under diminishing pressure.

Two main types of evaporators are in use having vertical and horizontal heating respectively. In the vertical type the apparatus (see Fig. 63) consists of a tall cylinder having at the bottom the heating space, which is made up of two horizontal iron plates perforated and fitted with two hundred to three hundred brass or copper pipes of about 30–55 mm. diameter and several wider circulation tubes. The whole forms a steam chest in which the outsides of the tubes are heated either by direct steam at  $1\frac{1}{2}$  atmospheres ( $112^{\circ}$  C.) in the first unit, or in subsequent units by vapour from the preceding units. The juice admitted below at about  $75^{\circ}$  C. is raised to boiling on entering the tubes, is forced up the narrow tubes, and down by the wider "circulators." The juice level ought to be such that on ebullition the froth overflows the top of the heating chamber. Concentrated juice passes from a valve in the bottom to the next unit. Disengaged air and ammonia pass off through a special tube. The steam from the boiling juice is deprived of sugar conveyed over by spirting by a dephlegmator in the upper dome and by inclined baffle plates in the horizontal drum connected therewith, whence the syrup returns to the evaporating space. The vessel is further fitted with observation windows, syrup level, and hydrometer test glass, manometer and thermometer.

In the **horizontal** or **Wellner-Jelinek** plant the steam traverses layers of horizontal tubes surrounded by the juice and passes backwards and forwards through the layers of tubes.

The vapours from the last unit are removed by **vacuum pumps**, where the steam is condensed by a spray of injected cold water, and the condensed water falls through a height of more than 30 ft., air being withdrawn by air pumps (Fig. 60).

Concentration is carried on to about  $60^{\circ}$  Balling for beet juice or 60 per cent. Brix for cane, and the quantity of water to be evaporated (W) may be calculated from the formula—

$$W = K \left( 1 - \frac{S_1}{S_2} \right),$$

where K = weight of juice and  $S_1$  and  $S_2$  initial and final gravities respectively.

Using steam at 1.5 atmospheres in the first unit, we have a temperature of  $112^{\circ}$  C., and if we have  $60^{\circ}$  as the boiling point in the last unit, the total fall is  $52^{\circ}$ , which is divided in multiple effect between the various units. Thus the temperature difference, *i.e.*, the difference between heating and evaporated steam, in each unit will be  $\frac{52}{n}$ , where  $n$  is the number of units. This fall is, however, not equal in practice, rising from the first to the last vessel.

Some data illustrating the process of multiple-effect evaporation, extracted from figures given by Jelinek for the horizontal system, are here tabulated.

It will be seen that the gain by adding units diminishes, and in practice generally triple and never higher than quintuple effect is used. The efficiency depends on the "coefficient of transmission," *i.e.*, the calories transmitted per minute per square metre of heating surface for  $1^{\circ}$  C. difference. For the horizontal system this has been ascertained at 22, for the upright at 15.

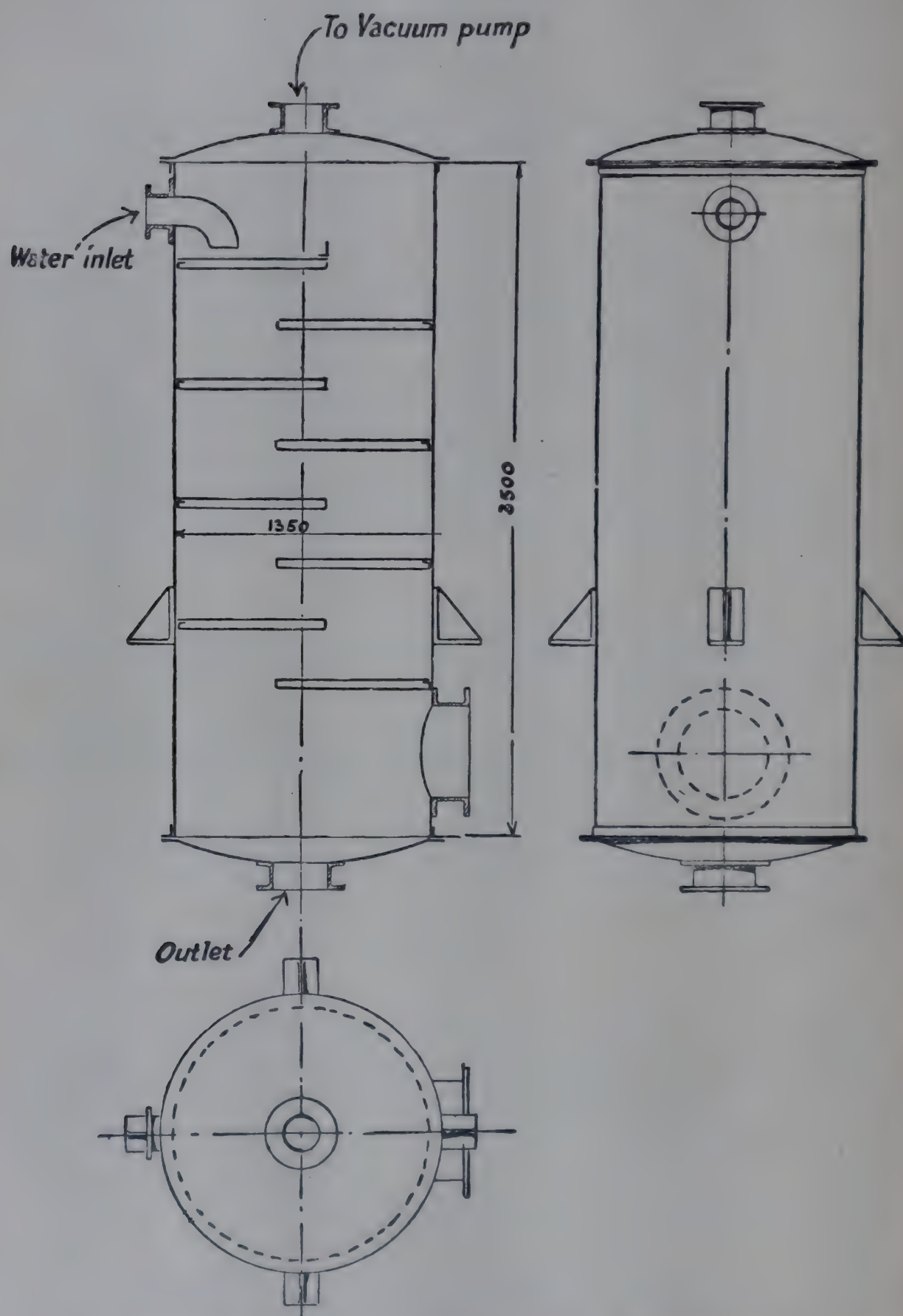


FIG. 60.—Barometric Cataract Contra-current Condenser. (Brand & Lhuillier, Brünn.)



	Simple Effect.	Double Effect.		Triple Effect.			Quadruple Effect.				Quintuple Effect.				
		I.	II.	I.	II.	III.	I.	II.	III.	IV.	I.	II.	III.	IV.	V.
Temperature of heating steam	112	112	86	112	94.6	77.4	112	99	86	73	112	101.6	91.2	80.8	70.4
Temperature of boiling juice	60	86	60	94.6	77.4	60	99	86	73	60	101.6	91.2	80.8	70.4	60
Pressure in millimetres.	152	456	152	648	318	152	733	460	266	152	804	553	367	239	152
Kilos steam condensed per hour per square metre	129.7	64.98	61.50	43.35	40.81	41.16	32.52	30.54	30.73	30.92	26.01	24.4	24.51	24.6	24.73
Kilos water evaporated per hour per square metre	124.8	61.50	62.28	40.81	41.16	41.52	30.54	30.73	30.92	31.11	24.4	24.51	24.6	24.73	24.74
1 kilo steam entering first vessel evaporates kilos water	0.9	1.96		2.85			3.79				4.72				
Kilos steam required to evaporate 100 kilos water	111.11	51.3		35.08			26.38				21.18				

The Kestner climbing film evaporator is now used to an increasing extent in sugar manufacture. A unit (see Fig. 60a) consists of a "calandria" composed of a shell or casing containing the evaporating tubes, which are 23 ft. long. The sugar

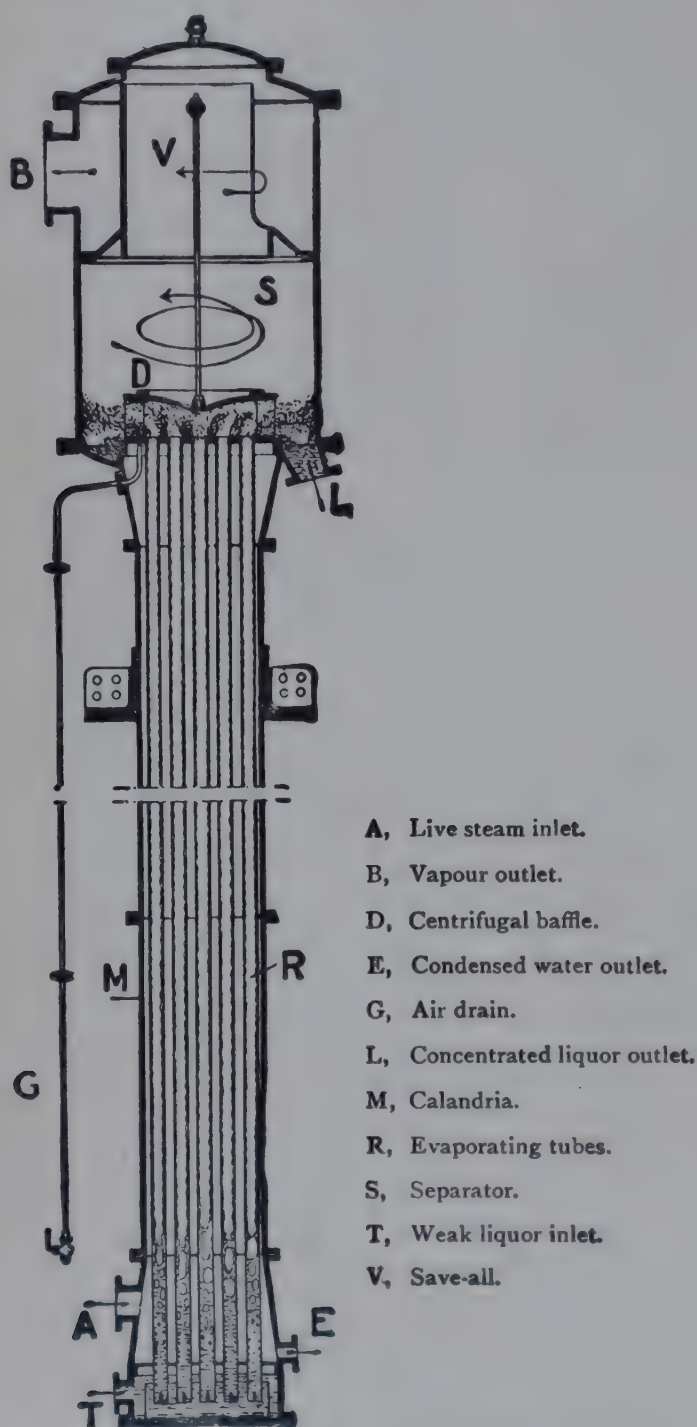


FIG. 60a.—Kestner Climbing Film Evaporators.

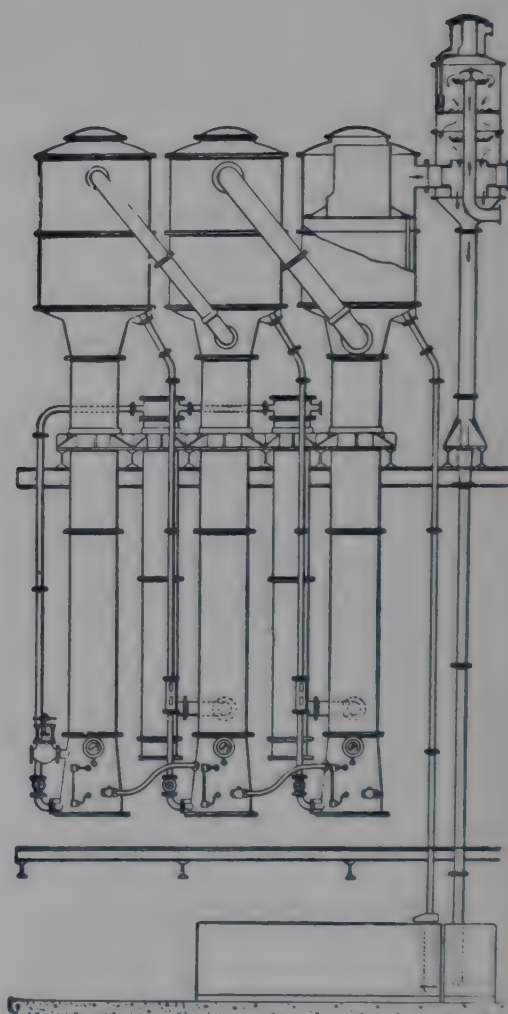


FIG. 60b.—Kestner Evaporators Used in Multiple Effect.

solution is fed into the apparatus at the lower inlet  $T$ , and passes from the feed box into the tubes. The steam or exhaust vapour (whichever may be the medium employed to heat the liquor) enters the calandria of the evaporator at  $A$ . The liquor boils in the tubes, a column of vapour rises up the tubes with a high velocity, and at the same time draws up a film of liquor on the inner surface of the tube.

Above the calandria is fitted the separator  $S$ , which consists of a cylindrical



vessel containing a centrifugal baffle placed immediately above the tubes, and so constructed that the liquor and vapour rising in the tubes up the calandria strike against the curved vanes of the baffle with a considerable velocity, thereby setting up a whirling motion which, by centrifugal force, effects a complete separation of the liquor from the vapour. The concentrated liquor passes down the outlet L, and the vapour, after first passing through the save-all, which is fitted in the upper part of the separator, leaves the separator at B. This vapour is usually used for passing into a second unit so as to obtain multiple effects in the usual way.

The velocity of the liquor through the tubes is so great that it only remains in contact with the heating surface for some few seconds before arriving at the

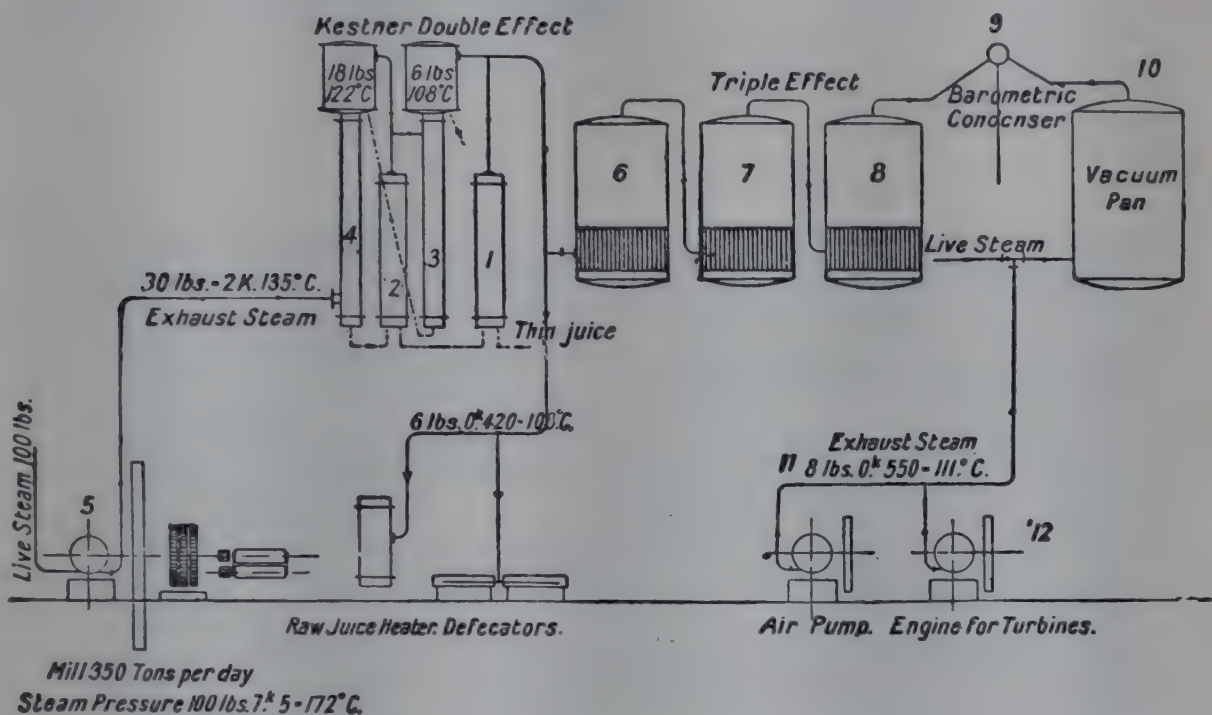


FIG. 60c.—Diagram of Evaporator for Working 350 tons of Cane per twenty-four hours.

separator. There is, therefore, no burning or coloration of the liquor. Also there is no "entrainment" (*i.e.*, escape or frothing over) of the liquor with the vapour.

Fig. 60b shows the method of connecting up Kestners for multiple effect.

Fig. 60c shows an illustration of two Kestners, one of which is used at the head of an existing ordinary triple vacuum pan so as to convert it into quadruple effect, while the other Kestner is used as a "pre-evaporator"—an application of the Kestner which is increasing.

The thin juice enters the heater 1, and is heated by steam coming from the Kestner 3. The thin juice then passes into the second heater 2, and is heated still more by the steam coming from the Kestner 4. Finally, the juice enters the Kestner 4, and is heated by exhaust steam at 30 lbs. coming from the mill engine 5. The juice passes from the Kestner 4 into the Kestner 3, and thence is either run off, or if necessary, passes into the triple evaporators 6, 7, and 8, where the final evaporation takes place. 9 represents the barometric condensation plant attached to the triple expansion pan, while 10 is another vacuum pan worked by exhaust steam coming from the air pump 11 and the turbine engine 12.



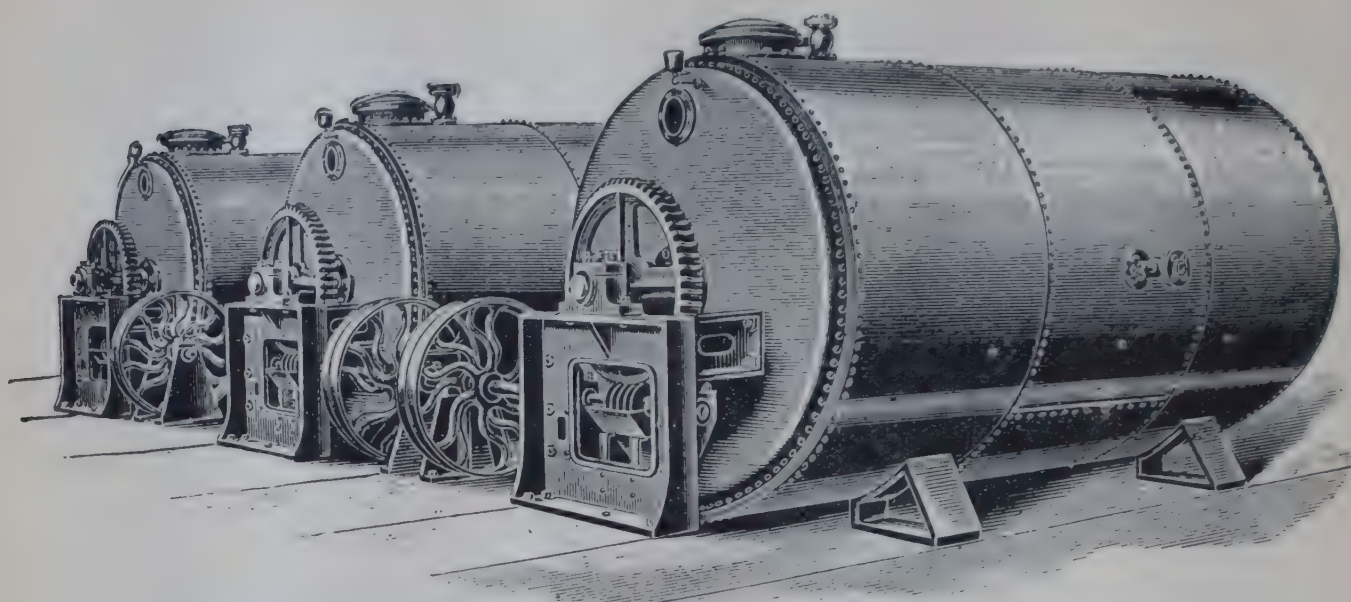


FIG. 61.—Closed Type Massecuite Receivers for Crystallisation in Motion.  
(A. & P. W. M'Onie, Glasgow.)

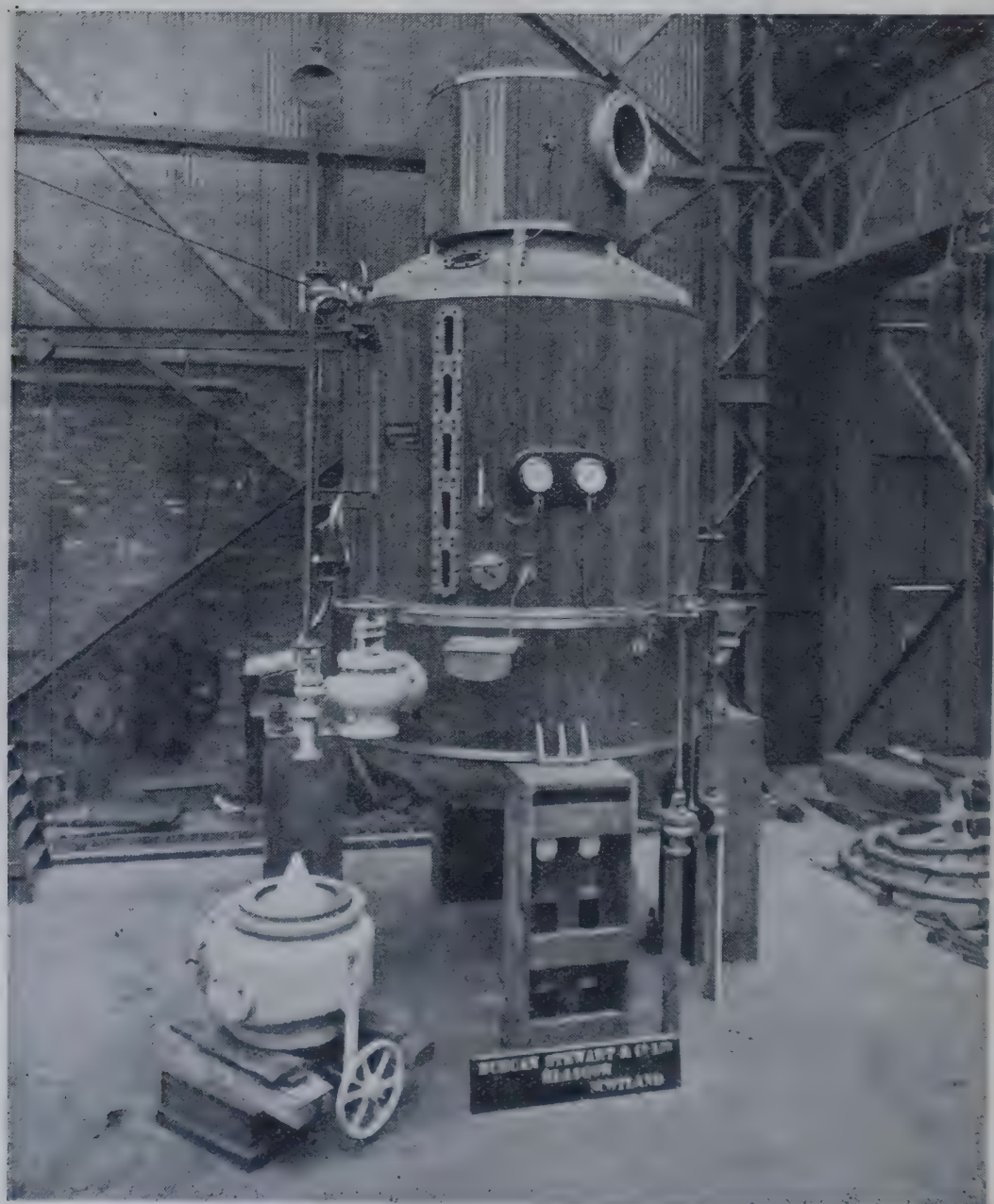


FIG. 62.—Crystalliser fitted with Harrison Cooling Gear.

*Vac Pan*



The saving in fuel achieved by multiple-effect evaporation is very great, about 80 kilos coal being required per ton of roots as against about 400 in the days of direct fire heating. It is a point, moreover, of special significance to the cane industry, which depends on exhausted cane or bagasse for its fuel.

During heating in evaporation there occurs with beet juice a notable decrease in alkalinity. This is due mainly to the disengagement of ammonia.

Juice of 12° Bg. usually has a phenolphthalein alkalinity of 0.015–0.02 per cent. reckoned as CaO, and on concentration to 60° Bg., instead of giving five times, it gives only about three times this value. Occasionally the decrease causes very bad boiling and discolouration, and may be corrected by addition of soda. Further, lime salts tend to separate on concentration, and form incrustations which seriously impair the efficiency of the plant. This may be overcome by promoting rapid circulation of the juice as in the special arrangement of the heating chest or calandria in the evaporators made by the Harvey Engineering Company of Glasgow (Fig. 63).

In many cases in the beet works the so-called middle juice, *i.e.*, juice from the last evaporator but one, of sp. gr. 30°–35° Bg., is saturated before further evaporation. This is done by joint carbonation and sulphitation to an alkalinity of 0.02–0.04 per cent. CaO, or by sulphitation to an equivalent degree. In any case such sulphitation is effected on the thick juice. In order to render the liquid more mobile for filtration it is raised to 95° C. before that operation.

Juice from cane which has been purified by defecation is difficult to filter, and is generally allowed to subside in eliminators at below 70°. These are rectangular or circular pans, having steam coils for the warming of the fluid. Sulphitation is often combined with elimination. Sand filters have been tried and are efficient, but have the defect of requiring much wash water. When, however, the cane juice has been carbonated it filters easily through ordinary filters.

**Boiling to Crystallisation, or Strike Point.**—Beet syrup of 60° Bg. is in this stage boiled to from 3.5–7 per cent. water content, these values showing the water content of the boiled mass, or "**massecuite**" (German, *Füllmasse*). The concentration of cane syrup is carried on the average to the degree shown by the composition:—

Sucrose	-	-	-	81.10
Glucose	-	-	-	6.93
Ash	-	-	-	1.12
Water	-	-	-	8.66

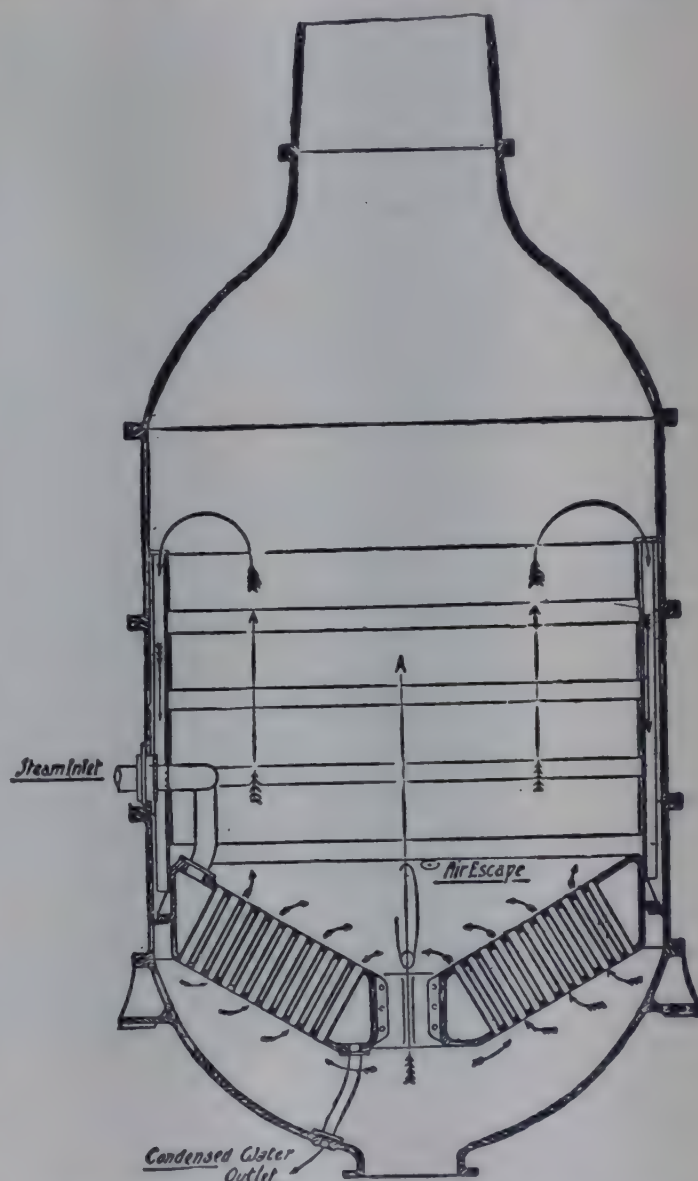


FIG. 63.—Harvey Patent Express Vacuum Pans.  
(Harvey Engineering Co., Glasgow.)



Boiling is effected in vacuum pans which in Austria are generally of the horizontal Lexa-Herold type, heated by brass steam tubes arranged in sections, which can be separately heated. Upright strike pans are also in use, and are general in cane boiling.

The principles governing the working of a vacuum strike pan are similar to those pertaining to the multiple-effect boilers. Steps must, however, be taken to secure effective circulation, which is more difficult with the thick mass of syrup and crystals than with the concentrated juice. This may be done by injection

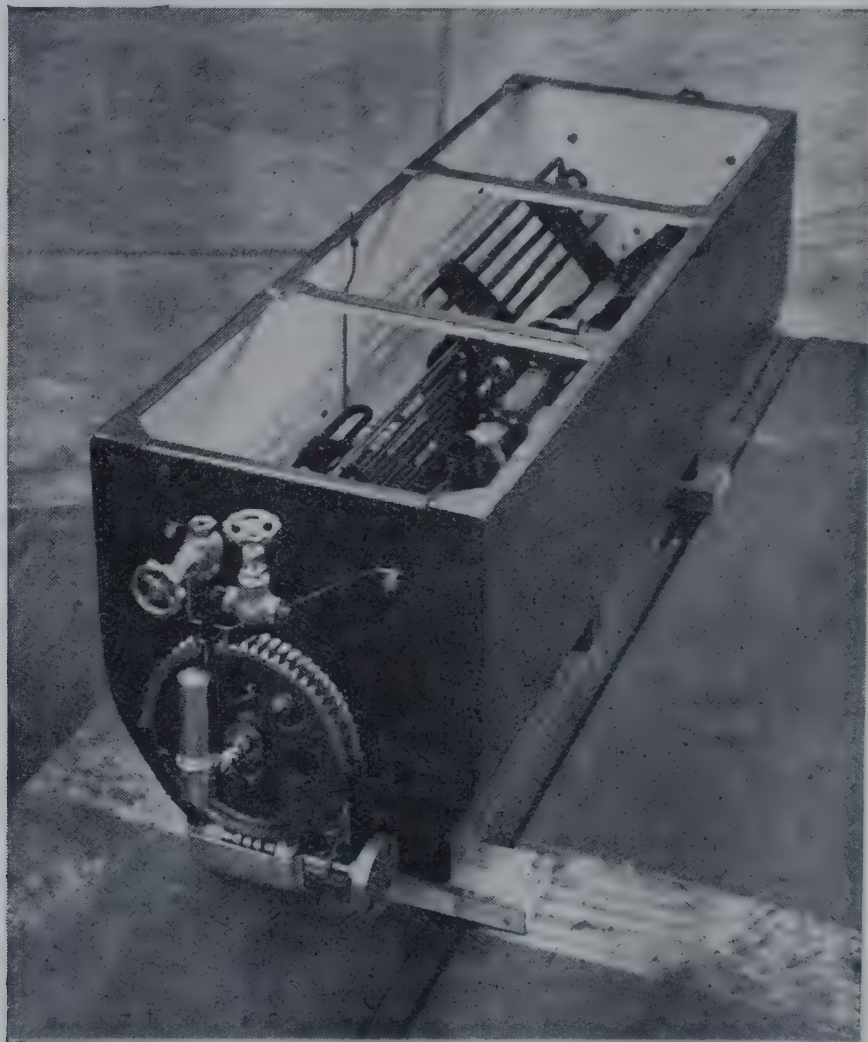


FIG. 63a.—Modern Vacuum Pan. *Crystallizer*

at the bottom of the boiling mass of dry steam. This does not impair the vacuum and secures mixture and steady boiling.

In the Harvey patent express pan (Fig. 63) the calandrias, or heating tubes, have an inclination which helps circulation, and this model further has a false lining which prevents return of condensed water. The addition of syrups or molasses should also be from below, which again helps effective circulation. An illustration of a modern vacuum pan is given in Fig. 63a.

The process of boiling falls into well-defined stages. At first we have concentration to thick syrup of about 80°. Then follows boiling to "grain," a most important stage, having for its object the formation of uniform crystals of such size as not to pass through or clog the meshes of the centrifugals. The supersaturated syrup is generally caused to grain or crystallise spontaneously, or by admission of fresh juice, which by promoting circulation, and still more by depressing the boiling temperature, induces rapid crystallisation in fine grains. The subsequent boiling has in view the growth of the already formed crystals and solution of the very fine



ones, and care is exercised to secure that a fresh small crystal formation or "false grain" shall not occur. Boiling is continued to a water content of 3.5-4 per cent. or 6-7 per cent., according as it is intended to cool at rest or in motion. The massecuite is discharged either into ordinary coolers or into special vessels designed for the very generally practised "**crystallisation in motion.**"

The crystallisers may be open or closed cylindrical vessels, and may or may not be jacketed for warm or cold water. They have shafts with blades, whose rotation keeps the mass in constant gentle motion. The modern types have hollow blades or coils in place of the blades through which cold and hot water may be passed if desired (see Fig. 62). This has the effect of causing the sugar separated on further cooling from the warm saturated solution to be deposited on the existing crystals, and not in the form of false grain throughout the mother liquor.

The very great solubility of sucrose will make it clear that the problem of a maximum crystallisation is one of great practical difficulty, having in mind the necessity of removing the molasses mother liquors which entangle the grain. Moreover the molasses contain uncrystallisable sugar held in solution by the salts on account of their so-called "**melassigenic power.**" (See pp. 142, 143.)

Geerligns defines **molasses** as: "A hydrated combination between sugar and salts, which cannot be broken up by dissociation in a concentrated state, and therefore cannot yield sucrose in a crystallised form." **Cane molasses** contains about 55 per cent. sugars (sucrose + invert), 20 per cent. water, and 9 per cent. ash.

**Beet molasses** contains about 50 of sugar, 10 of salts, 20 of water, 10 of nitrogenous and 10 of non-nitrogenous substances.

To facilitate **curing** or **centrifuging**, green molasses may be added to the massecuite, which will give sufficient mother liquor to secure the necessary mobility. Such added syrup will be recovered plus that due to the fresh massecuite, and is boiled down from time to time to sugar and exhausted molasses.

The "**absolute recovery**" method is of great value and interest, and an account condensed from Prinsen Geerligns is here given. The relation between the purity of the massecuite and the corresponding molasses cured hot is given by Pasma as:—

Massecuite of 90 purity yields molasses of 75 quotient.

"	88	"	"	71	"
"	85	"	"	65	"
"	82	"	"	62	"
"	80	"	"	60	"
"	70	"	"	50	"
"	65	"	"	45	"

If the syrup is over 80 purity it is reduced thereto by addition of green molasses of 60 purity, which will, as seen, again yield 60 molasses. On curing hot, first sugar and 58-60 molasses result. Sufficient of this molasses is then drawn into a second massecuite as to give a purity of 70, and this on boiling and hot curing yields first sugar and 48-50 molasses, which finally is used to reduce an 80 massecuite to 60, when, on high concentration and cooling, sugar and exhausted molasses result.

**Curing** or separation of crystals from the magma of crystals and molasses is effected in centrifugals.

Those of the Weston type are most usual. The spindle is suspended and driven from above by water turbine, or belt, or electrically, the power being applied accurately at the point of suspension. Vibration is reduced to a minimum by the conoidal rubber buffer, and discharge is effected below—a great saving in time and cleanliness. (Figs. 64, 65.) The centrifugals can make about 1,500 revolutions per minute, and may be arranged for continuous work.

From crystallisation in motion the viscid massecuite is centrifuged direct. If cooling has been done in tanks the hard massecuite is broken up in pug mills, and incorporated with the requisite molasses.

Centrifuging fails to absolutely separate the adherent molasses from the crystals, and these, therefore, are washed or "purged." This may be done by injecting a fine spray of water into the revolving machine, after the molasses has passed off, or by means of a jet of steam and air. The cleansing syrups inevitably dissolve some sugar, and are therefore collected apart from the molasses. Obviously, a pure concentrated sugar solution will be as effective to remove salts and non-sugars as water.

The product is usually machine dried in long inclined cylinders having scoops whereby the moist mass is turned over by the revolutions and meets a current of warm air, entering at about  $120^{\circ}$  and leaving at about  $50^{\circ}$ . Sometimes the sugar is dried by means of dry steam in the turbines.

Although pure sugar is not hygroscopic, there is often a coating of molasses which absorbs water, and under favourable temperature conditions affords a good medium for the growth of moulds and yeasts, whereby inversion and deterioration

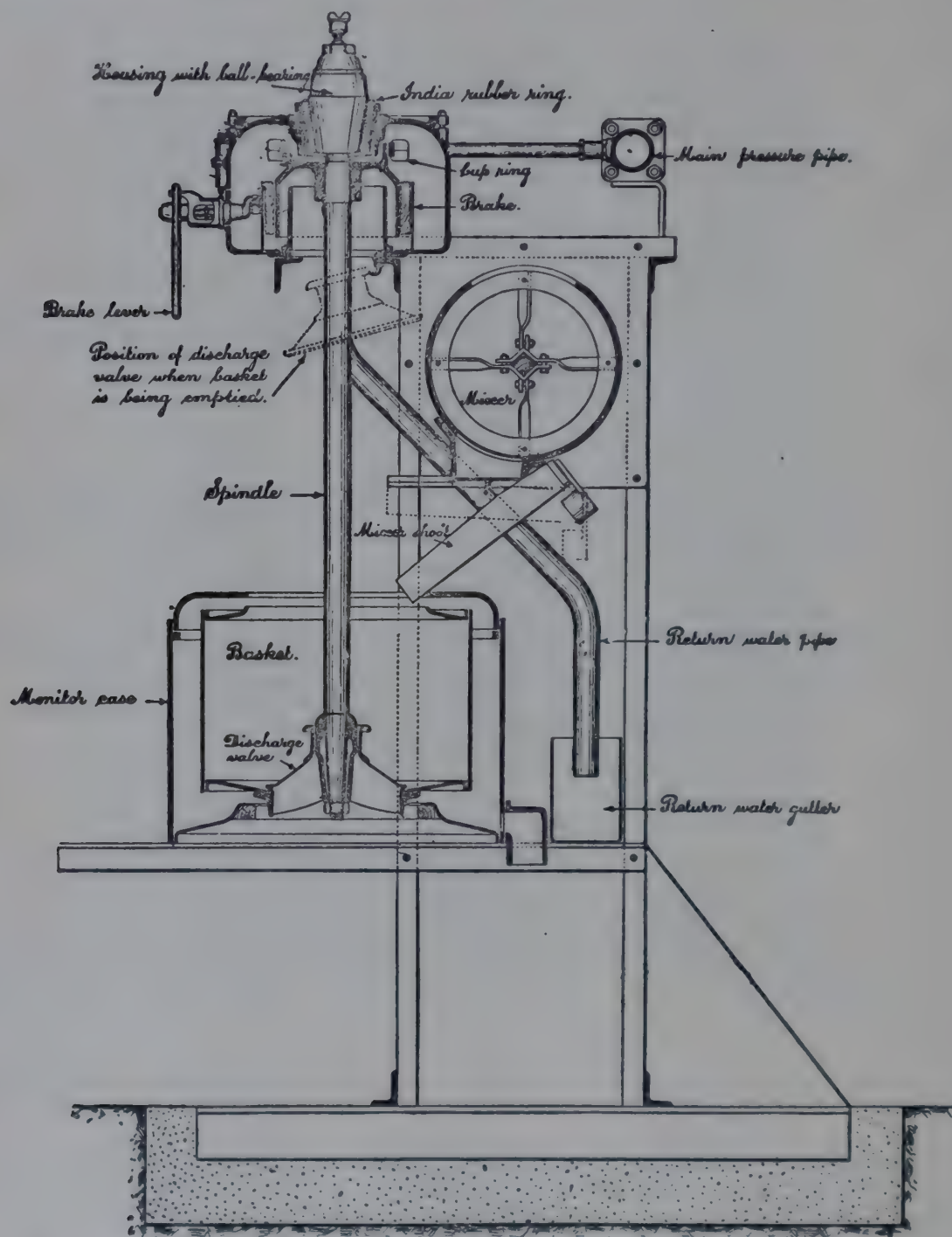


FIG. 64.—Patent Water-driven "Weston" Centrifugal Machine, showing Patent Steel Frame. (Messrs Watson & Laidlaw, Glasgow.)

is caused. In the case of cane sugar the presence of invert in the product and the warm moist climate render the material very prone to these changes. Close packing in bags of the dry cool product in stores capable of regulated ventilation or closing according to the hygrometric state of the atmosphere is recommended. Beet sugar is less liable to alteration, and is advantageously stored after artificial cooling. Alkalinity does not appear to be a certain safeguard, which is to be expected from the circumstance that alkaline media are most favourable to bacterial growth.



As regards the composition of raw sugar this naturally varies, beet being distinguished from cane by freedom from invert sugar. In the **commercial valuation** the polarisation *minus* ash  $\times 5$  *minus* invert is the basis for cane. For example, a sugar having  $97.0^\circ$  polarisation,  $0.85$  reducing sugar, and  $1.10$  ash, has the value  $97.0 - 0.85 - 1.10 \times 5 = 90.65$ . A beet sugar having  $94.95^\circ$  polarisation,  $1.04$  per cent. ash, and  $1.89$  per cent. organic non-sugar, would have the value  $94.95 - 1.04 \times 5 = 89.75$ , on the generally accepted standard that 1 part of mineral matter prevents the crystallisation of 5 parts of sucrose. Alternatively, beet is sometimes valued by deducting 2.25 times the joint ash and organic non-sugar; thus in the above case  $94.95 - (1.04 + 1.89) \times 2.25 = 88.36$ .

The final **exhausted syrups** or mother liquors form the **molasses**, the composition of which has been previously indicated. This was once an irksome bye-product, but to-day is used for various purposes, *e.g.*, in spirit manufacture, for instance West Indian rum; for making alcohol from beet molasses, (p. 293); for making trimethylamine (p. 376); for extraction of a further yield of sugar; for making cattle food preparations; or for direct feeding to the animals. Refined syrups, after inversion and clarification, form the **treacles** or **golden syrups** of consumption. Beet molasses is less pleasantly flavoured and more highly charged with salts. It is fed to the extent of about 30 per cent. to cattle in Germany and Austria, in rations of from 2 to 6 kilos per 1,000 of body weight per day, generally and advisedly in admixture with other foods or neutral bases such as peat. In England a mixture of molasses and peat moss is somewhat widely used under the name of "molassine meal." Owing to the high salt content irrational feeding with molasses is dangerous, causing digestive and urinary trouble, and animals need to be habituated to it by graded feeds. A similar preparation of cane molasses absorbed in the residual internal and finer fibre of the cane or bagasse is "molascuit." Both these are convenient and portable forms of food stuff.

### Separation of Crystalline Sugar from Molasses.

—Two main processes are available, *viz.*, **osmosis**, and precipitation either of **strontium**, or **calcium sucrates**. The **osmotic process** depends on the circumstance that the salts diffuse more rapidly through parchment paper into water than does the sucrose. In this way a partial separation is possible, incomplete, since obviously sucrose also will diffuse, though less rapidly.

The general arrangement of an osmosis plant is that of parallel flat chambers separated by

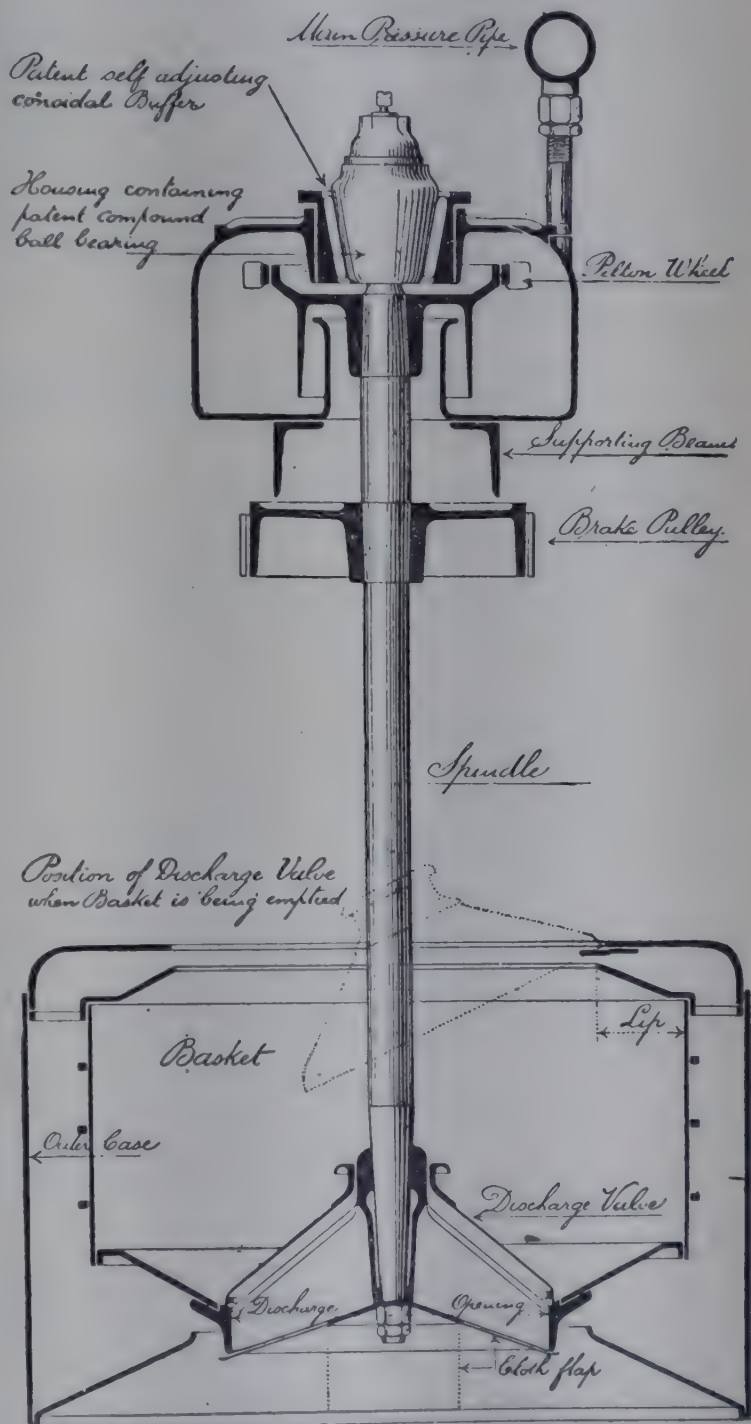


FIG. 65.—Section of a Water-driven "Weston" Centrifugal Machine.  
(Messrs Watson & Laidlaw, Glasgow.)



parchment paper, in which flow molasses and water in alternate chambers and opposite directions. The osmosed molasses is boiled to grain, and the resultant syrup re-osmosed until a final residual molasses which would not repay further osmosis is obtained. The osmosis water may be used as a fertiliser, or worked for spirit or potash. On 100 of molasses of 78° Balling about 15 per cent. of sugar may be recovered, having a quotient of about 95.

The separation by means of **strontia** depends on the formation of the sparingly soluble basic sucrate  $C_{12}H_{22}O_{11} \cdot 2SrO$ . In this process molasses and strontium hydroxide solution—eventually solid strontia—are boiled to an alkalinity of about 15-20 per cent.  $Sr(OH)_2$ , reckoned on the basis of 1 part sucrose to 2.5 parts crystallised  $Sr(OH)_2$ . The precipitate is rapidly filtered and washed with hot 12-14 per cent. strontia solution. On leaving at a low temperature ( $-10^\circ C.$ ) with a 2 per cent.  $Sr(OH)_2$  solution, the basic saccharate separates into crystalline hydroxide, and the sugar with half the strontia passes into solution. After separation the solution is saturated, and the sugar evaporated to massecuite. Strontium carbonate, and that recovered from the mother liquors, is reburnt, and the clarified mother liquors, after separation of strontia by carbon dioxide, are evaporated and burnt for potash.

In **Steffen's lime process** the sugar is precipitated by means of thorough agitation at not above  $20^\circ C.$  with finely powdered well-burned quicklime, as tribasic sucrate, which is used as a lime substitute in the treatment of diffusion juice.

**Refining.**—The technique of sugar refining varies according to the quality of the raw sugar, and the nature of the trade article which it is desired to turn out.

Raw cane or beet, or blends of both, may be operated upon, it having been claimed that the alkalinity of beet may correct the occasional acidity of cane.

On entering the refinery the raw sugar is sampled and stored, *e.g.*, in large bins, until required.

A preliminary curing in the turbine is sometimes resorted to, in the so-called *affination* process, and affination sugar is often used as an article of consumption, but naturally not of the first class. This treatment has the object of removing adherent impure syrup, which envelops the grain, and may be very dark coloured. In this syrup, obviously, the greater part of the non-crystallisable sugar and mineral matter is concentrated. The consistency of some raw cane, or muscovado, sugars does not permit of affination. When affination is feasible, the raw material is thinned by incorporation with a syrup of such strength as not to dissolve the crystals, but to merely act as a diluent of the adherent syrup. The mass is then turbinised, either in ordinary turbines (*q.v.*) or in open bottomed machines, in which an inverted cone on the spindle directs the magma, by centrifugal force, on to the basket of the turbine, where the same force holds it during spinning and purging, and on stopping the machine the sugar falls out by gravity, without handling.

It is dissolved, in blow-up pans, in such fashion as to give a solution of approximately 2 parts sucrose to 1 part water, and at this stage separated from coarser adventitious impurities.

The further purification consists in a preliminary treatment and a bone-charcoal filtration. After melting, the liquor is limed and carbonated, as in the carbonation process for beet and cane juices (see Fig. 65*a*). It is then filtered, either through plate and frame presses or sweetland filters.

After either filter-pressing, or filtration through bag filters, the clear juice is passed through the bone char filters.

Vegetable carbons are used also in place of bone char. These carbons, such as "Norit" and "Suchar," are mixed with the hot melt at carefully controlled pH and filtered. In some cases factories producing sugar from cane also refine their sugars. In one factory the carbon is produced from the press cake removed during the manufacture of raw sugar.

New animal charcoal contains from about 8-13 per cent. of carbon, 78.5-84 per cent. of calcium phosphate, 7.5-9 per cent. of calcium carbonate, and small quantities of alkalis, iron, and silica. The carbon of fresh char always contains fixed nitrogen and a little hydrogen, the former amounting to about one-twentieth of the total carbonaceous matter, and diminishing on repeated reburning. It is possible that the nitrogenous matter plays an important part in the special decolourising action, which is not understood. It is, however, known that pure vegetable



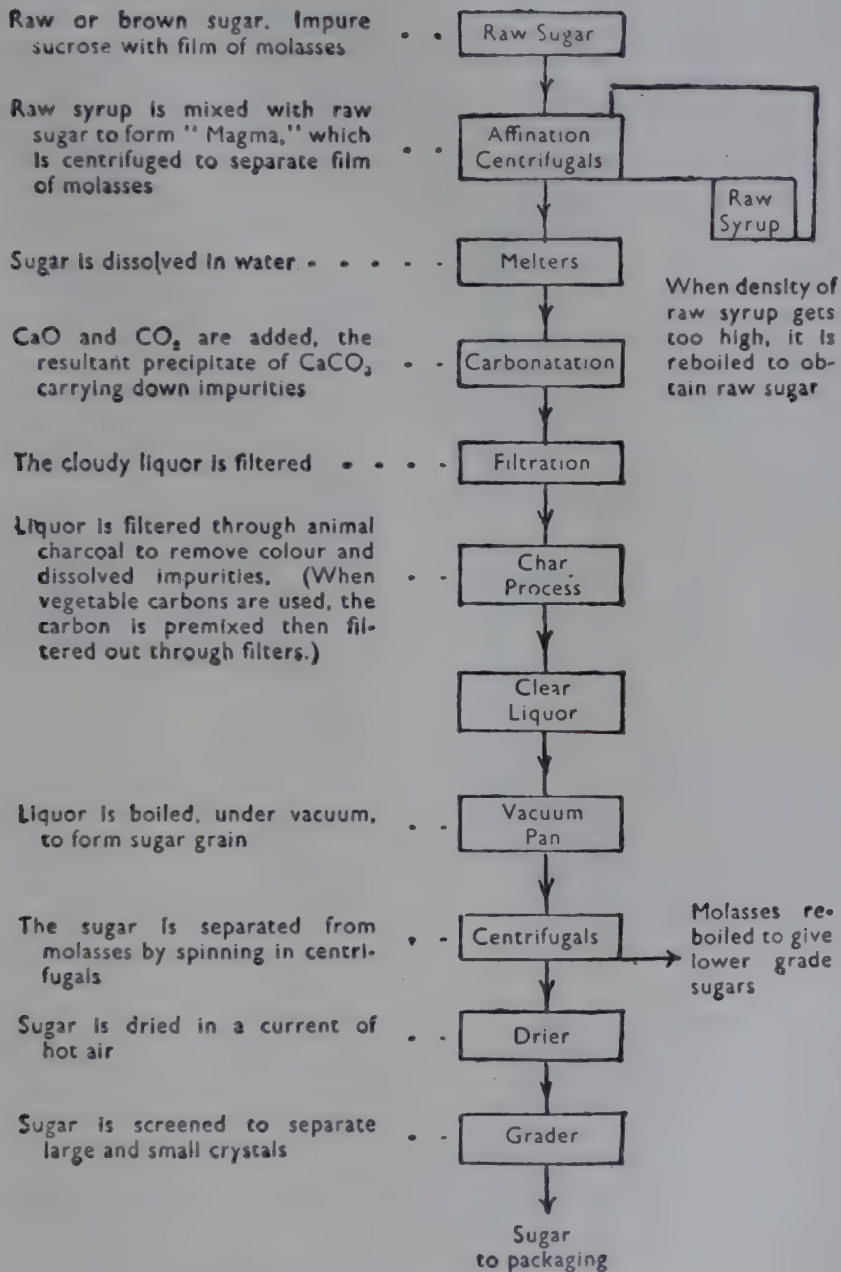


FIG. 165a.—Refined Sugar Diagram

charcoal does not possess this property in the same degree, though bone char freed by means of acid from calcium salts is very efficient. Traces of ammonia and of calcium sulphide may be present, which are obnoxious, and are to be got rid of by washing and reburning.

The **char filters** have commonly the form of iron cylinders of varying dimensions, which may hold upwards of 20 tons of char, the grain of which is also

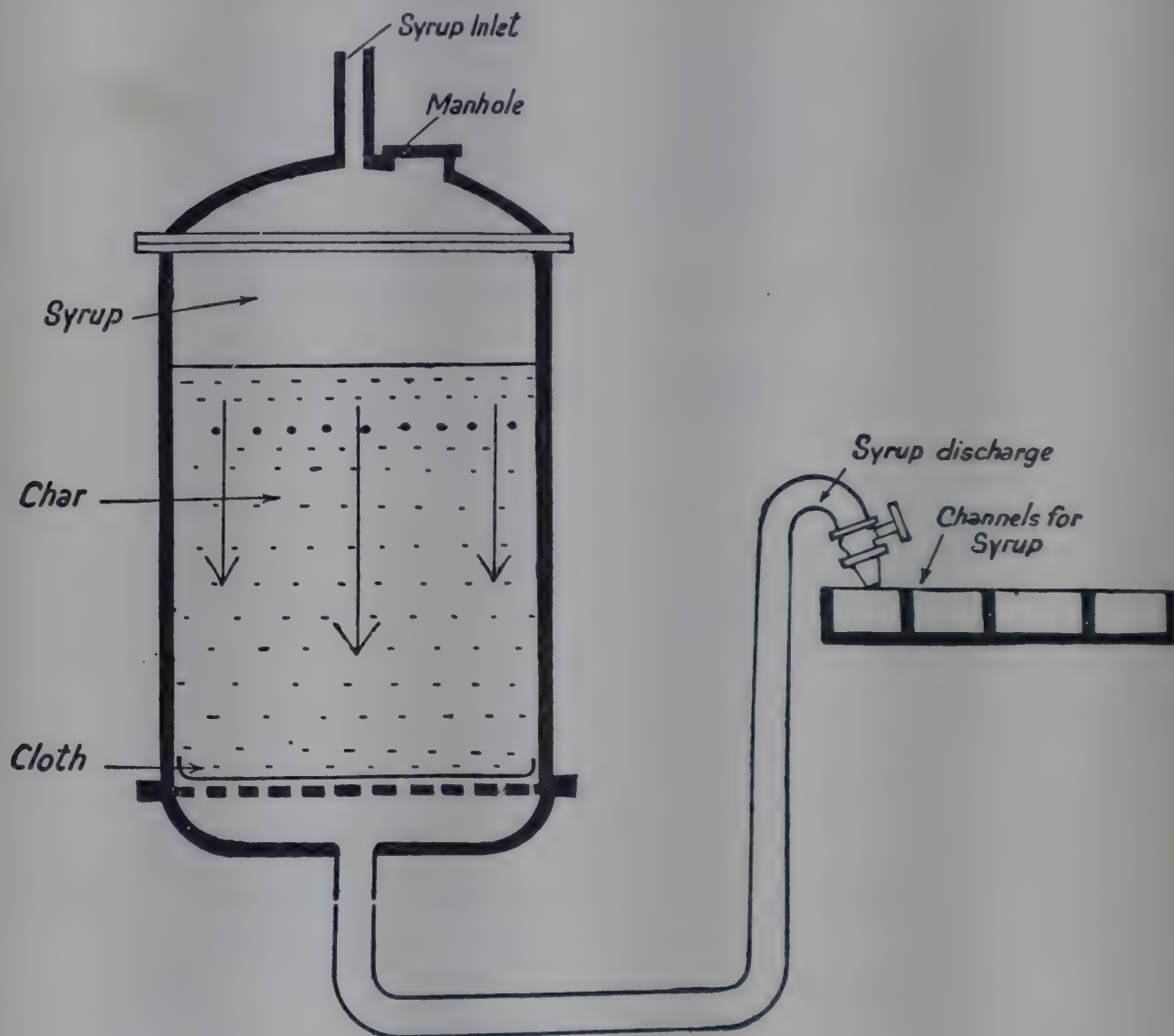


FIG. 66.—Char Filter.

very variable, a 20/30 sieve size being not uncommon. The char is uniformly packed on the filter cloth (see Fig. 66), and the solution passes evenly through the mass, at a temperature of  $68^{\circ}$ – $70^{\circ}$  C., is drawn off, as shown, and the filtrate collected, according to colour, in channels or gutters. At first water white, the filtering syrup eventually becomes yellow, at which point the char is thoroughly washed till free of sugar, and then copiously with water to remove soluble impurities absorbed from the sugar solution, dried, and reburnt.

The **charcoal kilns** usually consist of oval pipes arranged vertically in a furnace in three rows on each side. The char, entering from above, is thus submitted to strong heat or dry distillation, whereby the organic impurities are expelled without loss of carbon. It passes downwards at a speed, capable of regulation by the discharge valves, depending on the temperature of the furnace and the order of proximity of the row of pipes to the fire. The pipes are continued downwards through the kiln floor, and thus serve as air coolers, whereby loss of carbon by ignition on emerging from the pipes is prevented. The effective life of the char is long, and may extend over several years.

A new process which utilises the decolourising action of chlorine is used by some factories which produce refined sugar on the cane plantation. The sugar, after affination is melted, and rapidly stirred. A mixture of a high grade bleaching powder and soluble phosphates is mixed, which releases the chlorine and at the same time forms a precipitate of calcium phosphate. This precipitate is filtered, the decolourised sugar dechlorinated by means of hydrogen peroxide, and the clear white solution is ready for crystallisation in the vacuum pans. An added advantage



of this process is that it produces a sterile sugar, free from bacteria or yeast, and is therefore ideal for use by fruit canners.

The art of **sugar boiling** in refinery work reaches a very high level, demanding a long apprenticeship. The object is to obtain a uniform grain of a size governed by the nature of the desired finished article, and the boiling is done in vacuum pans (*vide supra*). Having obtained a crystallisation, or grain, great care is required in the introduction of fresh syrup, to ensure that the number of crystals shall not increase, but that those first formed shall grow in size, and that fresh crystal formation or "false grain" shall not occur. False grain formation is especially objectionable in boiling lower massecuites, for its appearance very much interferes with the turbinizing of the crystals from the surrounding molasses.

When boiling has reached the required point the product may be directly turbinized, or further crystallised in motion, in which the existing crystals grow at the expense of the sugar of the cooling saturated mother liquor.

**Granulated Sugar** is prepared by passing the turbinized and washed wet product through granulators, long revolving cylinders, inclined at about  $20^\circ$ , in which the mass is propelled and disintegrated by revolving arms. In the reverse direction there passes a current of warm air to dry the crystals, which are then sieved on vibrating tables, or other types of mechanical sieve.

For the manufacture of **cube or "loaf" sugar**, so named from the now obsolete loaves or cones into which sugar was formerly moulded, is in many modern works prepared by special processes, of which the Adant may serve as an illustration. A series of detachable iron frames is built up so as to form rectangular moulds about 1 in. thick, arranged radially around the periphery of a hollow cylinder, which is then placed into a well-fitting containing ring. Massecuite, discharged into a heated reservoir vessel, is then run in until the moulds are full. After cooling, the moulds have the consistency of a dense mass of crystals in a thick syrup, and the inner ring is detached, by the aid of a compressed air blast, and transferred to a centrifugal of heavy type. Therein the sugar is freed, *in situ*, from syrup, and washed. On taking the form to pieces, complete rectangular slightly wedge-shaped tablets result, which after drying are machine-cut to the form of cubes or otherwise as may be desired.

We are indebted for diagrams, and desire to express our thanks therefor, to the following firms:—

Action Gesellschaft für Maschinenbau, vormals Brand & Lhuillier, Brünn, Austria; Maschinenfabrik Büttner, Verdingen am Niederrhein, Germany; The Harvey Engineering Company, Glasgow; Messrs A. & P. W. M'Onie, Glasgow; Messrs Watson & Laidlaw, Glasgow; Messrs Duncan Stewart & Co. Ltd., Glasgow.

### Glucose, Dextrose, or Starch Sugar

**Glucose**,  $C_6H_{12}O_6$ , forms the crystalline hydrate,  $C_6H_{12}OH_6O_2$ , which melts at  $86^\circ$  C. and of which 97.8 parts are dissolved by 100 of water at  $15^\circ$  C. It is very soluble in methyl alcohol. Glucose displays mutarotation, a freshly prepared cold solution having  $[\alpha]_D + 105$ , which decreases rapidly on heating to the final equilibrium value  $+ 52.85$ .

Alkalis isomerise glucose, yielding an equilibrium mixture of glucose, fructose, and a little mannose, also produced similarly from fructose, but alkalis at the same time break down glucose, yielding complex organic acid salts.

Glucose is oxidised by Fehling's solution, as also are maltose and fructose; yields an osazone (M.P.  $205^\circ$ ) also given by mannose and fructose; and with  $\alpha$ -naphthol and sulphuric acid gives a red colour, a reaction which is not characteristic, being given also by sucrose and other sugars.

**Manufacture.**—Commercially glucose is manufactured from starch by heating with dilute mineral acids, when hydrolysis ensues:—



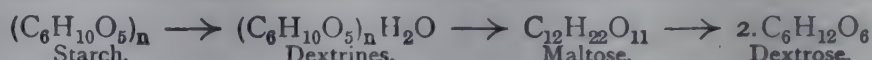
Mixed with a large amount of dextrine it comes into commerce: (1) as solid glucose, (2) as the viscid syrup known as "starch syrup."



The industry is of Continental origin and dates from the time when cane sugar was excessively dear, so that efforts to produce a substitute from starch had some possibility of success. At the present time, however, glucose is valued not as a substitute for sucrose but rather for the presence of certain dextrines in the commercial product, which are: (1) valuable food stuffs, (2) are soluble, (3) will not crystallise, (4) are non-fermentable. Such glucose is largely used: (1) as a malt substitute in brewing: the dextrose ferments to alcohol, and the unfermentable dextrines increase the percentage of extract in the beer; (2) for the manufacture of glassy sweets, cane sugar being unsuitable for the purpose; (3) for adding to honey; (4) for use in confectionery, cakes, preserves, jams, jellies, syrups, etc.

The great drawback to the use of glucose is its want of sweetness, being only two-thirds as sweet as sucrose. The addition of saccharin or other artificial sweetener is illegal in some countries.

The hydrolysis of starch by dilute acids is a complex change (see Starch), the starch first breaking down into dextrines which then break down into maltose, and this finally into dextrose. The saccharification only proceeds easily in very dilute solutions, as shown in the following scheme:—



In practice, the starch is intentionally left incompletely hydrolised, the presence of dextrines being essential. Moreover, in the concentrated solution some of the dextrose molecules condense together to produce gummy dextrine-like products called 'glucosines.' Simultaneously a certain amount of "isomaltose,"  $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ , a sugar isomeric with maltose, but not fermentable by yeast or hydrolysable by enzymes, is also produced. The rate of hydrolysis of the different acids varies considerably, the stronger acids having a more rapid action than the weaker; thus, taking the hydrolysing power of an equivalent weight (36.5 g.) of HCl as 100, the following table expresses the hydrolysing power of the *equivalent weights* of some other common acids:—

Acid.	Equivalent Weight.	Hydrolysing Power.
Hydrochloric acid, HCl . . . . .	36.5 g.	100
Sulphuric acid, $\text{H}_2\text{SO}_4$ . . . . .	49 g.	70
Nitric acid, $\text{HNO}_3$ . . . . .	63 g.	100
Tartaric acid, $\text{C}_4\text{H}_6\text{O}_6$ . . . . .	150 g.	2.5
Formic acid, $\text{H.CO}_2\text{H}$ . . . . .	46 g.	1.6

The starch is placed in a boiler, a small percentage (say  $\frac{1}{4}$  per cent. or even less) of HCl or  $\text{H}_2\text{SO}_4$  or HF is added and the whole heated under 1-2 atmospheres pressure, cooled, and the acid neutralised. If HCl is employed it is neutralised with  $\text{Na}_2\text{CO}_3$ , the small percentage of NaCl produced being imperceptible to the taste;  $\text{H}_2\text{SO}_4$  is neutralised with  $\text{CaCO}_3$ , the  $\text{CaSO}_4$  produced coming down as a precipitate. HF is completely precipitated as  $\text{CaF}_2$ .

**Starch Syrups.**—Moist potato-starch, carefully purified from nitrogenous matter (the presence of which yields a dark product), is used. 200 parts of water and as much  $\text{H}_2\text{SO}_4$  as serves to make a 0.3 per cent. solution are placed in a boiler, and 100 parts of the starch (weighed dry) made into a milk with water are run into the boiling acid, so that the starch is almost immediately gelatinised. The mixture is then heated in a copper autoclave for one hour under 1 atmosphere pressure, so that about a half of the starch is hydrolysed to dextrine and the rest to dextrose (or maltose). The process is ended when a test portion gives no coloration with iodine—showing that all the starch has disappeared. The product is a non-crystallisable syrup having a density of  $17^\circ$  Bé. = about 30 per cent. of carbohydrate. The sulphuric acid is neutralised with  $\text{CaCO}_3$ , the solution filtered from the  $\text{CaSO}_4$  through a filter-press, evaporated to  $32^\circ$  Bé. in a vacuum pan, again filtered from precipitated  $\text{CaSO}_4$  through a filter press, and finally decolourised by filtering through animal charcoal, which simultaneously absorbs some of the finer particles of  $\text{CaSO}_4$ . The syrup is now again concentrated in vacuum pans to  $42^\circ$ – $45^\circ$  Bé. and should be clear and colourless.



A good concentrated syrup should be so viscid at ordinary temperatures that it scarcely flows; it should not become cloudy on standing and should bear a temperature of  $140^{\circ}\text{C}$ . without darkening in colour. The product, after heating to  $140^{\circ}$  and cooling, should solidify to a glassy mass, which is used for making sweets. It has only a moderate degree of sweetness.

**Solid Glucose** is manufactured in the same way as the syrup, but the hydrolysis in the autoclave is carried on for a longer time so that the resulting mixture contains almost twice as much dextrose as dextrine. The product, when filtered, decolourised and evaporated, solidifies as a white mass of microscopic crystals, in which fine needles of dextrose hydrate,  $\text{C}_6\text{H}_{12}\text{O}_6 \cdot \text{H}_2\text{O}$ , may be seen embedded in syrup. The crystalline dextrose hydrate, however, cannot be separated by ordinary means from the syrup. The following shows the composition of a starch syrup and of solid glucose thus manufactured:—

	Syrup.	Solid Glucose.
Dextrose - - - - -	40-43 per cent.	55-61 per cent.
Dextrine - - - - -	41-46 „	24-30 „
Water - - - - -	15-19 „	15-20 „

A certain amount of “maltose” is always present. The maltose and dextrose together constitute the fermentable portions of the mass, the dextrines (which include isomaltose and glucosines) the non-fermentable portions.

It has not yet proved possible to manufacture pure dextrose on the industrial scale, since neither the crystals of the hydrate  $\text{C}_6\text{H}_{12}\text{O}_6 \cdot \text{H}_2\text{O}$ , nor those of the anhydride, can be easily centrifuged from the adhering syrup. Some American firms, however, evaporate the dextrose solution *in vacuo* until it is of the proper consistence; then crystals of pure dextrose,  $\text{C}_6\text{H}_{12}\text{O}_6$ , are stirred in, and the mass crystallises out as a mass of grains, which are then centrifuged and obtained in a colourless state. A very large amount of a dark-coloured syrup is produced in this process, which is sold to brewers for colouring porter, under the name “Climax Sugar.”

**Caramel, Burnt Sugar, Gravy Salt, Gravy Colour, and Coleurs for Soups, Wine, Beer, Vinegar, Sauces, etc.**, are manufactured on a large scale from dextrose by making its solution alkaline with soda, evaporating, and heating to  $220^{\circ}\text{C}$ . The dark brown mass is poured into tins and allowed to solidify. Sometimes it is sold dissolved in a little water. Much used for colouring sweets, liquors, etc.

Asrylmusry gives the following recipe for making a colour for rum:—3 kilos of NaOH or KOH, 6 kilos water (or 4 kilos sodium or potassium carbonate and 8 kilos water) are dissolved by heating in a large iron pan, and then 120 kilos of glucose (or 130 kilos of syrup of glucose) are added, and the whole is heated over a direct fire until irritating vapours begin to be evolved. The heat is decreased, and the mixture stirred continually until the proper shade of colour is attained. 30 or 40 l. of water are then added in a fine jet. To produce a colour for vinegar, we take 6 kilos ammonium carbonate, 6 kilos of water, and 120 of glucose, and proceed as before.

**Caramel from Cane or Ordinary Sugar.**—The sugar is heated with continual stirring in an iron pan until the whole melts, turns brown, and suddenly begins to froth up. Not more than 15 per cent. of weight of sugar should be expelled, or the product will become insoluble. The change is stated to be represented by the equation:— $11\text{C}_{12}\text{H}_{22}\text{O}_{11} = \text{C}_{125}\text{H}_{188}\text{O}_{80} + 7\text{CO}_2 + 27\text{H}_2\text{O}$ . Cane sugar caramel is an amorphous reddish brown brittle mass, M.P.  $134^{\circ}$ - $136^{\circ}\text{C}$ .; completely soluble in water, only partially so in alcohol. Bitter taste. Nonfermentable.

### Invert Sugar and Honey; Laevulose

**Invert Sugar** is the mixture of glucose and fructose resulting from the hydrolysis of sucrose. It is manufactured from sucrose by heating in solution with small quantities of mineral acid. It is laevorotary, the laevo-rotation of fructose (laevulose) being greater than the dextro-rotation of glucose, and has  $[\alpha]_D^{20} = -(27.9-0.32t)$ , consequently, on inversion dextro-rotatory sucrose becomes laevo-rotatory. A mixture of laevulose and dextrose and a little sucrose occurs in the juices of many fruits—especially grape juice, which is quite free from sucrose. The mixture is



known as "grape sugar." Invert sugar, however, is never obtained commercially from plant juices after the manner of sucrose, because it is too soluble and too difficult to crystallise.

It is always manufactured by heating a 75-80 per cent. sucrose solution with a very small amount, say 0.02-0.05 per cent., of hydrochloric acid, or 0.2 per cent. of tartaric, citric, or formic acid, to 95°-100° C. and neutralising with soda. The resulting syrup must not be concentrated in the usual way or it browns, and consequently is sold as it stands. If it contains 75 per cent. or under of sugar it will not crystallise; syrups with 80 per cent. of sugar on cooling separate as a solid mass. This invert sugar is used for improving wine musts (see **Wine**); it is also used in making artificial honey, since it is chemically identical with honey, failing only the flavouring matters peculiar to that fluid.

**Honey**, in fact, is simply a mixture of dextrose and levulose, together with a little sucrose, dextrines, flavouring matters, pollen, and a little free formic acid, which acts as a preservative. In granular honey the crystals are of dextrose. When bees are fed on sucrose or glucose these materials pass over unchanged into the honey, except that some of the soluble salts are retained, resulting in a lower ash figure in the honey than in the original sucrose or glucose.

In making artificial honey, invert sugar prepared as above is mixed with about 25 per cent. of a natural honey, rich in flavouring matters.

Since the invert sugar contains sucrose, dextrose, levulose, and even dextrine, in amount almost the same as they occur in natural honey, the mixture has practically the same chemical and physical properties as real honey, and, in fact, cannot at the present time be distinguished from it. An adulteration of honey with dextrose from starch is easily detected, because of its strong dextro-rotary properties.

**Pure Levulose** (fructose, fruit sugar) is obtainable from **inulin** — the laevo-rotatory starch of **Dahlia**, **Inula**, and **Chicory** — by heating with dilute acids in exactly the same way that dextrose is obtained from ordinary starch. Laevulose is sweeter than cane sugar, and is very soluble in water, but difficult to crystallise. It is easily decomposed by acids into non-crystallisable syrups. It reduces Fehling's solution very easily and ferments directly with yeast. It is strongly laevo-rotatory, the rotation being greatly effected by the concentration ( $c$ ) of the solution and the temperature;  $[\alpha]_D^{20} = -(91.90 + 0.111c)^\circ$ . Industrially laevulose is obtained from invert sugar by means of the difficultly soluble calcium laevulate. It could, however, be obtained on the large scale from **dahlias** (containing 12 per cent. inulin) or chicory.

**Milk Sugar, Lactose**,  $C_{12}H_{22}O_{11}$ , is manufactured from the whey left over during the manufacture of cheese. See under Milk, p. 78a.

### Other Varieties of Sugar

**Maple Sugar** is obtained to the extent of 15,000 tons yearly in Canada and North America from the juice of the maple tree. In spring the mature trees (which may be 200 years old) can be made to yield sap containing about 2 kg. of sugar. The sap contains 2-4 per cent. of sugar, principally sucrose. It is consumed locally as a syrup. The industry is decaying, but maple sugar is highly valued for its flavour.

In the East Indies about 140,000 tons of sugar are made annually from the juice of the coco-palm and similar sugar palms. In Bengal great plantations of the palms exist, each palm yielding during the interval of twenty-five to thirty years about 38 kg. of sugar annually. The labour of cultivation is very small. The sugar is consumed locally.

Attempts to cultivate the **amber cane** (*Sorghum saccharatum*) in the United States for sugar have proved a failure, because besides sucrose the juice contains much invert sugar and non-saccharose constituents, so that it is difficult to get the sugar to crystallise out in sufficient quantity to repay working.



### Estimation of Sugar

Invert sugars may be estimated volumetrically by the Eynon-Lane method, which uses Fehling's solution, the copper in the solution being reduced by the invert sugar. Methylene blue is used as an indicator. Full methods are given in "Spencer and Meade's Handbook" or any modern publication for the sugar chemist.

**Sucrose** or cane sugar does not reduce Fehling's solution, but when hydrolysed by warming with dil. HCl it is converted into a mixture of dextrose and levulose (see **Invert Sugar**), which has the same reducing power as glucose—342 g. cane sugar = 360 g. invert sugar or glucose.

When the cane sugar solutions are fairly pure the amount of sugar is immediately given by the specific gravity with a floating hydrometer. The following gives the sp. gr. at 20°/20° C.

Per Cent.	Specific Gravity.	Per Cent.	Specific Gravity.	Per Cent.	Specific Gravity.	Per Cent.	Specific Gravity.
0	1.00000	19	1.07844	38	1.16833	57	1.27123
1	1.00389	20	1.08287	39	1.17341	58	1.27703
2	1.00779	21	1.08733	40	1.17853	59	1.28286
3	1.01172	22	1.09183	41	1.18368	60	1.28873
4	1.01567	23	1.09636	42	1.18887	61	1.29464
5	1.01965	24	1.10092	43	1.19410	62	1.30059
6	1.02366	25	1.10551	44	1.19936	63	1.30657
7	1.02770	26	1.11014	45	1.20467	64	1.31260
8	1.03176	27	1.11480	46	1.21001	65	1.31866
9	1.03586	28	1.11949	47	1.21538	66	1.32476
10	1.03998	29	1.12422	48	1.22080	67	1.33090
11	1.04413	30	1.12898	49	1.22625	68	1.33708
12	1.04831	31	1.13378	50	1.23174	69	1.34330
13	1.05252	32	1.13861	51	1.23727	70	1.34956
14	1.05677	33	1.14347	52	1.24284	71	1.35585
15	1.06104	34	1.14837	53	1.24844	72	1.36218
16	1.06534	35	1.15331	54	1.25408	73	1.36856
17	1.06968	36	1.15828	55	1.25976	74	1.37496
18	1.07404	37	1.16329	56	1.26548	75	1.38141

A rapid way of estimating sugar is by the polariscope. The solution is clarified with aluminium sulphate or lead acetate, filtered, and its rotation taken in a 20 cm. tube.  $[\alpha]_D^{20}$  for cane sugar = 66.4 (see p. 142). If  $m$  = mass of sugar in 1 c.c.,  $\alpha$  = observed angle of rotation, and  $l$  = length of tube in dms., then  $m = \frac{\alpha}{l} \times \alpha_D$ . If there are other optically active substances besides sugar

present, the polarisation angle, after inversion with HCl, is also taken, and the alteration in the angle of rotation gives a clue to their amount and nature. In technical analysis the scale is not graduated in arc degrees, but so as to indicate per cent. sucrose direct, when the normal weight, dissolved in 100 c.c., is observed in a 20 cm. tube. The German normal weight of sucrose is 26.048 g., and the graduations arc degrees Ventzke; the French instrument reads degrees Laurent for a normal weight of 16.33 g.

1° Ventzke = 1.5931, Laurent = 0.3440 arc. 1° Laurent = 0.6277, Ventzke = 0.2167 arc.

If clarification is necessary, *e.g.*, in beet valuation, the readings must be corrected for dilution consequent on the addition of basic lead acetate, or if 10 c.c. of this solution is added to 100 c.c. of extract the sugar may be read direct in a 22 cm. tube. For details regarding the estimation and testing of sugar the reader is referred to standard treatises mentioned at the beginning of the article.

## II. SACCHARINE AND OTHER ARTIFICIAL SWEETENING CHEMICALS

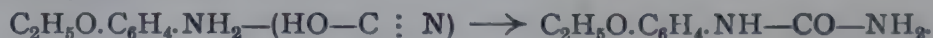
By G. MARTIN, Ph.D., D.Sc.

Within the last few decades chemicals of enormous sweetening power have been placed on the market. The most important of these is the **Saccharine** of Fahlberg, *o*-anhydrosulphamine-benzoic acid or benzoic sulphimide,

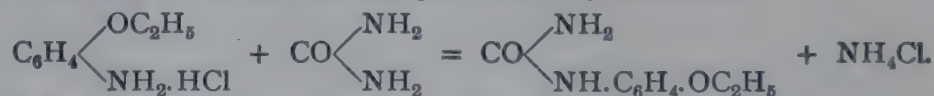
$\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CO} \\ \text{SO}_2 \end{smallmatrix} \text{NH}$ ; discovered in 1879 by Ira Remsen and C. Fahlberg, and now manufactured by Fahlberg, List, & Co., in Salbke-Westerhüsen near Magdeburg. **Toluene** is converted into *o*- and *p*-toluene-sulphonic acid,  $\text{C}_6\text{H}_4(\text{CH}_3)(\text{SO}_3\text{H})$ , by treating with concentrated  $\text{H}_2\text{SO}_4$  at  $100^\circ \text{C}$ . The acid is converted first into the calcium salt (by  $\text{CaCO}_3$ ) and then into the sodium salt (by  $\text{Na}_2\text{CO}_3$ ), which is dried, treated with  $\text{PCl}_3$  and  $\text{Cl}$  gas, whereby toluene sulpho-chloride,  $\text{C}_6\text{H}_4(\text{CH}_3).\text{SO}_2\text{Cl}$ , is produced. This, by treating with  $\text{NH}_3$  gas or with  $\text{Am}_2\text{CO}_3$ , yields *o*-toluol-sulphamide,  $\text{C}_6\text{H}_4(\text{CH}_3).\text{SO}_2\text{NH}_2$ , which is oxidised by an alkaline solution of  $\text{KMnO}_4$  to  $\text{C}_6\text{H}_4(\text{COOK}).\text{SO}_2\text{NH}_2$ , which when treated with  $\text{HCl}$  is immediately converted into free *o*-sulphaminebenzoic acid,  $\text{C}_6\text{H}_4(\text{COOH}).\text{SO}_2\text{NH}_2$ , which then spontaneously splits off water, forming the anhydride,  $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CO} \\ \text{SO}_2 \end{smallmatrix} \text{NH}$ , which separates out.

Saccharine is a white crystalline powder with difficulty soluble in water, melts at  $223.5^\circ \text{C}$ . and is *five hundred times* sweeter than cane sugar. **Easily soluble saccharine** consists of the sodium salt,  $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CO} \\ \text{NH} \end{smallmatrix} \text{N}.\text{Na}$ , prepared by treating saccharine with alkali carbonates.

**Dulcin** or **Sucrol** is another sweet chemical, about two hundred times sweeter than cane sugar. It is mono-*p*-phenetol-carbamide,  $\text{NH}_2.\text{CO}.\text{NHC}_6\text{H}_4.\text{OC}_2\text{H}_5$ , prepared by evaporating a solution of *p*-amidophenetol cyanate thus:—



It may also be obtained by heating urea with phenetidine hydrochloride,



White needles, M.P.  $173^\circ \text{C}$ .; soluble in 800 parts of cold or 55 parts of boiling water, also in 25 parts of alcohol.

Other very sweet chemicals are **Glucine** (amidotri-azinesulphonic acid or its Na salt), **Sandoce** or

**Methyl Saccharine**,  $\text{C}_6\text{H}_3(\text{CH}_3) \begin{smallmatrix} \text{CO} \\ \text{SO}_2 \end{smallmatrix} \text{NH}$ , etc.

Saccharine and similar sweetening chemicals possess no food value at all, while sugar, on the other hand, is a valuable food. The use of saccharine has on this account been made illegal in many countries as a sweetening agent for cakes, liquors, etc., intended for human consumption (except in the case of certain medicines). Saccharine must be made under Government supervision, and it is sold by apothecaries to diabetic patients as a substitute for sugar. It has considerable antiseptic or preserving qualities.

Saccharine is subjected to a duty of 7d. the oz. in Great Britain. No saccharine was manufactured in the United Kingdom prior to 1903.

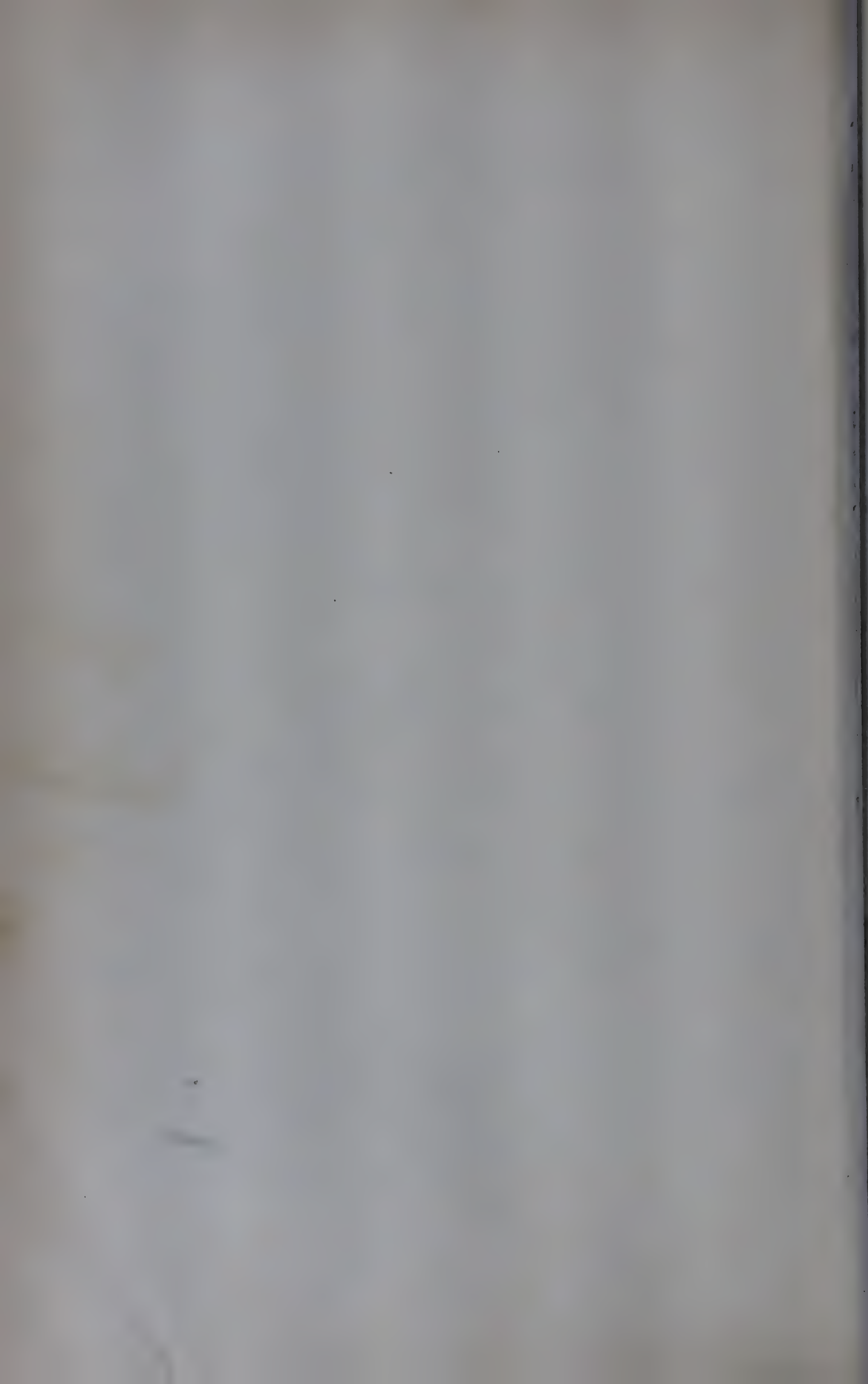
For modern statistics see Appendix III.



### SECTION III

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## The Starch Industry





# THE STARCH INDUSTRY

BY G. MARTIN, Ph.D., D.Sc.

REVISED BY E. I. COOKE, M.A., B.Sc., A.R.I.C.

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**Starch**,  $(C_6H_{10}O_5)_n$ , is a white, glistening, tasteless carbohydrate, found in the form of small granules in the cells of grain, legumes, and potatoes. It is, next to cellulose, the most abundant material found in the vegetable world, existing in all plants with the exception of the fungi.

Starch is a condensation product of low grade sugars (hexoses), and is originally formed in the cells of the leaves of plants from the  $CO_2$  of the air, by the aid of chlorophyll in the presence of sunlight. The starch is a migratory reserve food material, being transformed by enzymes into soluble sugars, which pass into the sap of the plant, and so it is carried throughout the plant, building it up and appearing at different stages of plant growth as cellulose, gum, lignin, etc. The microscopic starch granules have a concentrically stratified structure, similar to that of an onion. According to older ideas (Nägeli), the granules are surrounded by a sheath of cellulose, and growth occurs in concentric new layers from the kernel outwards. According to modern ideas (A. Meyer, “Untersuchungen über die Stärke,” Jena, 1895), the starch granules are spherocrystals, which grow from the centre outwards in the usual manner in the form of a cone-shaped agglomerate of fine crystalline needles, which branch off like trees, and thus extend their growth. The formation of concentric layers is due to the varying density and moisture-content of the different zones.

As regards the chemical nature of starch, Brown and Morris (see pp. 264, 265, *Beer*) consider it to have the formula  $5(C_{12}H_{20}O_{10})_{27}$ . According to Maquenne and Roux (*A. ch.*, [8], 9 (1906), 179-220), **Natural Starch** consists of two distinct substances, **Amylose** (80-85 per cent.) and **Amylopectin** (20-15 per cent.), the first being identical with Nægeli’s and Brown and Heron’s starch cellulose. **Amylopectin** is identical with Nægeli’s “starch granulose.”

**Kinds of Starch.**—Starch is generally obtained in Europe from potatoes, rice, wheat, and maize. In the tropics it is obtained from the palm, and tubers of various plants, *e.g.*, **sago starch** is obtained from the pith of the sago-palm (*Sagù lævis*, etc.), **arrowroot** is the starch of the *Maranta arundinacea* and *indica* (West Indies, Brazil, etc.). **Tapioca** comes from the *Manihot utilissima*, Pohl. Every species



of starch exhibits its own particular form and structural markings, so that adulteration can be detected and measured (*e.g.*, the admixture of cheap potato starch with expensive wheaten or rice starch) by microscopical examination. Each starch cell has a dark point, central in some, eccentric in others, known as the *hilum*. Round this are a series of concentric lines which give each kind of starch grain a characteristic appearance. (See Fig. 67, p. 178.)

**Potato Starch** has the largest granules (0.05–0.09 mm. diameter), of a characteristic mussel-like appearance.

**Wheaten Starch** consists of round lens-shaped cells of 0.020–0.030 mm. diameter, with a central dark point and faint markings. Mixed with these are still smaller cells, 0.002–0.008 mm. **Maize Starch** consists of characteristic polyhedral cells, 0.015–0.020 mm. diameter, with a dark centre and no visible layers.

**Rice Starch** consists of very small sharp-cornered almost crystalline-looking granules, of diameter 0.003–0.007 mm., which agglomerate together to larger granules. **Tapioca**, **arrow-root**, and other forms of starch have all their characteristic appearances, easily recognised by experts as the result of microscopical and optical investigation (see Fig. 67, p. 178).

**Properties.**—Starch is a very inert body, insoluble in cold water, alcohol, ether, and cuprammonium (the latter differentiating it from cellulose). It dissolves in KOH solution, forming a potassium derivative. Starch is very hygroscopic, retaining when air-dried from 16–28 per cent. of water, and when dried in a vacuum it retains about 10 per cent. Absolutely dry starch attracts moisture with great avidity, becoming warm when moistened. When dry, starch may be heated without change to 149° C. (300° F.), but between 149° and 204° C. (300°–400° F.) it is transformed into **dextrine** or **British gum** (which see), a substance soluble in cold water. At higher temperatures the starch is decomposed.

Although insoluble in cold water, starch granules, when heated with water, swell up and form a paste, and in the presence of much water produce colloidal solutions. The temperature at which this “gelatinisation” occurs differs with the various kinds of starch, *e.g.*, potato starch gelatinises with water at 65° C., maize starch at 75° C., barley, kilned malt, rice, rye, and wheat starch at 80° C., while green malt and oat starch gelatinise at 85° C. The paste from wheaten and maize starch has a far greater “sticking power” than that from potato starch. The sticking power is increased by slowly drying the starch at a low temperature, and reduced by the presence of acids or alkalies and by prolonged boiling.

In general, when starch is heated alone or under pressure with water, the starch molecule breaks down into “dextrines,” which are permanently soluble in cold water. This is a consequence of progressive “hydrolysis,” water being gradually combined as the breakdown of the starch molecule proceeds. This conversion proceeds especially rapidly under the influence of dilute acids or diastase, the dextrines having the composition  $(C_6H_{10}O_5)_n \cdot H_2O$ . The first product of the transformation is “erythro-dextrines,” and which give a red or brownish colour with iodine; as the hydrolysis proceeds, the iodine coloration vanishes, achro-dextrines being produced; the final product of the action of diastase on starch is **maltose**,  $C_{12}H_{22}O_{11}$ . Acids hydrolyse the maltose further into two molecules of **glucose** or **dextrose**,  $C_6H_{12}O_6$ . This reaction is used for manufacturing glucose or dextrose from starch (see **Glucose**, p. 166).

### Manufacture of Starch

It will be noticed that cereals of various sorts contain far less water than potatoes. Maize and oats are richest in fat. Regarded as a diet the cereals contain a large excess of carbohydrate and a deficiency of protein and fat. Bread and cooked cereals, however, are eaten, not as a source of protein, but as a source of **carbohydrate**, and as a diluent to the concentrated protein and fat foods. Of the cereals **wheat** and **rye** alone are suitable for making bread, on account of containing a peculiar protein, “glutin,” which becomes viscid when mixed with water, and causes the binding properties of the dough.

The following table shows the percentage of starch in the chief raw products used in its manufacture:—



	Rice (husked).	Wheat.	Maize.	Potatoes.
	Per Cent.	Per Cent.	Per Cent.	Per Cent.
Starch (inclusive of sugar and dextrine)	76-80	70.0	68.5	20.0
Cellulose fibre, pentosane, etc. - -	0.6	2.5	2.5	0.8
Nitrogenous substances - - -	7.8	12.4	9.9	2.0
Fats - - - - -	0.5	1.7	4.6	0.2
Ash - - - - -	1.4	1.8	1.5	1.0
Percentage of dry substance -	86-90	88.4	87.0	24.0

**Rice Starch.**—Rice, *Oryza sativa*, contains a higher percentage of starch (76-80 per cent.) than any other grain, but, on account of the extreme minuteness of its starch granules, and the presence of gums and albumens which firmly cement the cells together, is one of the most difficult substances to work for pure starch. For this reason the operation is usually undertaken only by very large industrial manufactories, and bruised rice is usually employed.

The process is as follows:—The rice is soaked with a very dilute solution of NaOH (0.3-0.6 per cent. solution, a stronger solution gelatinises the starch) in large cemented tanks. This dissolves the gums and nitrogenous matter cementing the starch cells together. The wet rice is then finely ground between millstones, keeping it moist during the process with NaOH solution. The grinding finally disintegrates the agglomerate of starch cells into the individual cells. The mass is next transferred to vats provided with stirring apparatus, and a milky suspension of the fine starch particles is obtained, the cellulose, fibres, and heavier constituents sinking to the bottom. The starch milk will not easily and quickly deposit the starch by sedimentation (as is the case with potato starch), on account of the extreme smallness of the rice-starch granules. Consequently to extract the starch, the milky liquid is transferred to rapidly rotating centrifugals, the drums of which are *not* perforated to allow the water to escape. As the result of the centrifugal force, the starch granules settle out as a compact ring on the interior circumference of the rotating drum, the outermost layers being practically pure starch, while the internal part of the ring is composed of impure starch, mixed with cell fragments of mixed starches. In the middle of the drum the water settles out as a clear liquid; this is run off, and the compact ring of starch is taken out, and the interior impure layer scraped off and made to undergo the same process again. It is usually necessary to add a trace of ultramarine to the starch in order to obtain a pure white. The starch is then cut into 7-in. cubes, pressed in iron forms until the water content is diminished to 45 per cent., and then slowly dried in drying chambers. When the amount of water reaches 29 per cent. the surface layer of starch is scraped off. This layer is of a yellowish colour and contains a considerable quantity of impurities which have diffused out with the water from the interior of the cake to the exterior, and been left behind by the evaporating water. The residual cake of starch is now packed in cardboard or paper boxes, and dried until peculiar longitudinal fissures or cracks appear. It has then 12 per cent. of water.

During the process of drying great care must be taken to guard against the development of *moulds* on the surface of the starch—a result of the incomplete separation of the nitrogenous matter—such moulds often completely spoiling the goods.

The alkaline liquid or “lye” separated from the starch during the grinding and soaking process contains a considerable amount of nitrogenous matter in solution. The dissolved matter is precipitated by  $H_2SO_4$  as a glutinous mass, which, when dried, forms a valuable cattle food. The other waste liquids from the manufacture are valuable manuring waters for meadow lands, and are used as such. Their escape into small streams is dangerous.

Rice starch has great sticking power, and is nearly twice as valuable as potato starch (*q.v.*). On account of the smallness of its grains it may be used in a powdered form for stiffening linen in laundry work.

**Wheat Starch.**—A grain of wheat consists of (1) the germ, (2) the endosperm or kernel, (3) the outer envelope or husk, which constitutes the bran. The husk has an outer cuticle from which delicate hairs spring, under which are three other layers, the two outer of which consist of flattened cells. Then comes the envelope of the seed, the “testa” or “episperm,” which encloses the endosperm (see Fig. 68).

The envelope of the seed consists of angular cells filled with a mixture of soluble and insoluble proteins, which with water form a thick viscid mass, and when dried has a horny appearance. This is the “gluten,” and its presence determines the binding quality of dough made from wheaten flour or rye. The gluten does not exist as such in the grain or flour, but is developed by the interaction in the presence of water of two proteins, gliadin and glutenin.



The **endosperm** consists of (A, Fig. 68) large starch cells provided with delicate walls, and filled with starch granules.

The husk ("bran") consists principally of cellulose with pigments and mineral matter. The endosperm is mainly starch. The germ (B, Fig. 68)—forming only a small proportion of the whole—is rich in protein and fat. For **chemical composition** of wheat, see p. 178.

For the preparation of flour the grain is ground or milled in iron roller mills and the various constituents of the grain separated. The outer coats yield **bran, fine pollards, sharps, and middlings**; the **endosperm** yields ordinary wheaten flour; the germ is removed as "offal."

The flour is sorted out by machinery into—

(1) A smaller portion of very white flour known as "patents." It is very poor in proteins and is the flour from which genuine Vienna bread and the best fancy breads and pastries are made.

(2) A larger portion known as "bakers' flour."

The **semolina**, which is obtained from the central part of hard wheat and which is rich in gluten, is also removed from white flour.

Hence ordinary white flour (and white bread made from it) contains no bran, germ, or semolina, and consequently valuable food constituents (mineral matter and protein from the semolina and bran, protein and fat from the germ) are absent from it.

Wholemeal flour (and wholemeal bread) includes these constituents, and is consequently much richer in nitrogenous and mineral foods than white bread. Wholemeal bread, however, irritates delicate stomachs on account of the cellulose and silica of the outer coat.

Recently the outer layers of the husk have been removed, and with it the irritant material, and a flour has been put on the market containing the valuable mineral, protein, and fatty constituents of the inner branny coat, germ, and semolina. This is the so-called "80 per cent. flour" and is used in making "Standard bread." By "80 per cent. flour" is meant that from 100 lbs. normal wheat (*i.e.*, 1 bushel weighing 64 lbs.) 80 lbs. of flour are obtained.

The food known as **Grape-Nuts** is derived solely from **cereals**, the constituents of which are rendered more digestible than in the raw cereal (probably by a process of malting followed by roasting). This is evident from the remarkable solubility of the preparation, nearly 50 per cent. of which is soluble

in cold water. The soluble portion contains no starch, being chiefly dextrine. The following gives an analysis of a sample of "Grape-Nuts": moisture, 6 per cent.; mineral matter, 2 per cent.; fat, 1.6 per cent.; proteids, 15 per cent.; soluble carbohydrates, etc., 49.4 per cent.; unaltered insoluble carbohydrate, 26 per cent.; the mineral matter is rich in phosphoric acid. It is placed on the market by the Postum Cereal Co. Ltd., Battlecreek, Michigan.

The process now usually adopted for working wheaten flour for pure starch is the *Sweet Process*. The flour is mixed with a small amount of water to a stiff dough, placed in special kneading machines, and the excess of water kneaded out. Most of the starch goes into suspension in the water, forming a milk, while the sticky gluten and cellulose fibres remain behind as a thick soft mass. The open kneading machine most used for the process is seen in the illustration. It consists of a trough in which two kneading arms are worked in opposite directions, one directly by means of a pulley and the other indirectly by means of toothed wheels. The wings revolve at different rates, so that no clogging can occur. The starch milk is

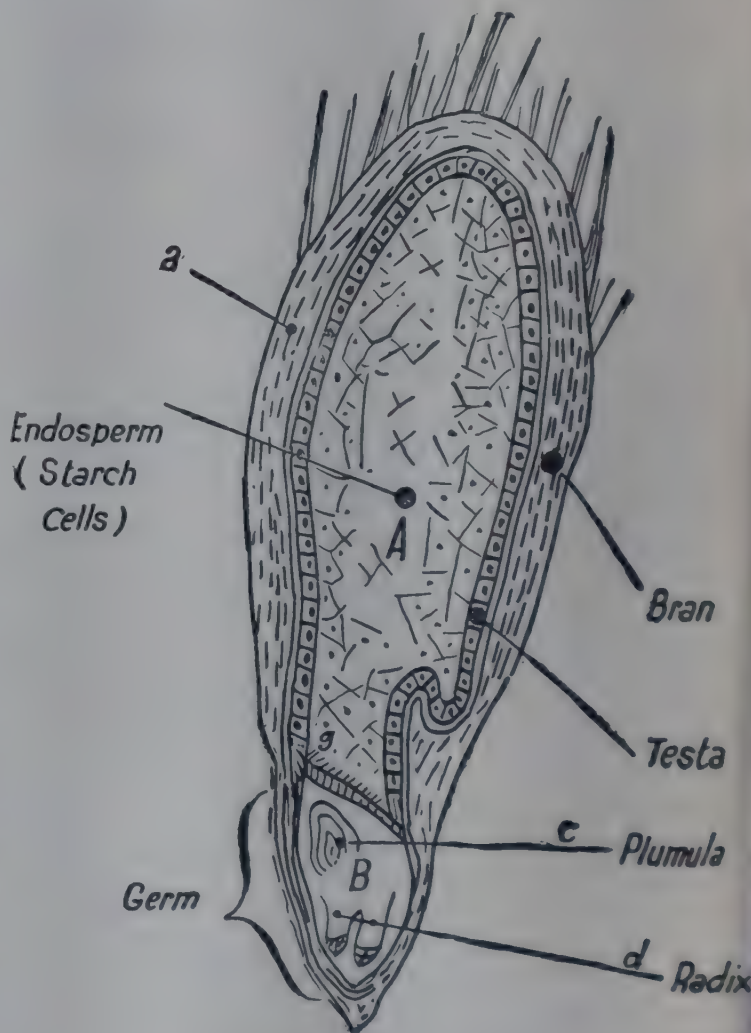


FIG. 68.—Wheat Grain.



emptied out of the trough from time to time, the last traces being removed from the remaining gluten by passing the mass through rollers.

The starch milk is separated into pure "Prima" starch and glutinous "secondary starch" by centrifugalling in special drums, which are non-perforated, the process being exactly the same as described in the manufacture of rice starch. The drying is also carried out as with rice starch, similar fissures making their appearance in the dried mass as is the case with rice starch, the fissured appearance differentiating the valuable wheaten and rice starch from the cheaper potato starch. Even on adding glutinous material to potato starch it is impossible to obtain this fissured appearance.

The gluten-rich secondary starch is either directly used as food (also as cattle food) or is allowed to spontaneously ferment at 50° C. (see below) when a further yield of starch is obtainable.

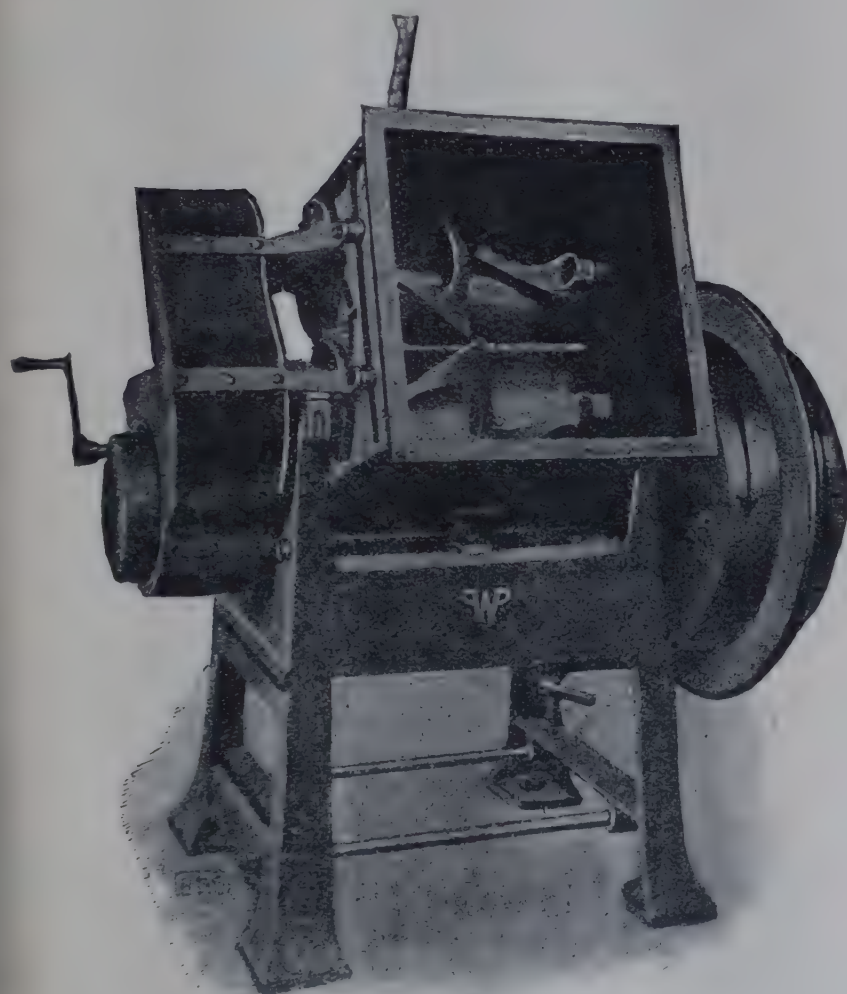


FIG. 69.—Kneading Machine.  
(Werner, Pfeleiderer, & Perkins, Peterborough.)

In Germany wheaten starch factories are often run directly in connection with a bakery. The flour is kneaded out with water and the starch milk is separated as above described and worked for pure starch by means of centrifugals. In this way, 60-75 per cent. of pure starch is obtained. The glutinous residues are then used for baking.

With proper care 100 parts of flour yield 60 parts pure "prima starch," 10 parts "secondary starch," and 10 parts of the sticky gluten. The gluten is difficult to completely dry, and being a proteid, in a wet condition rapidly undergoes putrefaction. In a dried and powdered condition attempts have been made to place it on the market under various tradenames, *e.g.*, "Albumen Powder," "Aleuronate," etc., but with little success. Usually it is allowed to putrefy at about 50° C. for some time, when it acquires gummy properties, and is

then rolled out into thin sheets, dried, and sold as a paste called "**Shoemakers' Paste.**" No other paste adheres so well to leather as this paste, and with it leather can be secured not only to leather but also to woven materials, paper, etc.

Formerly, and to some extent at the present time, crushed wheat was worked for starch by moistening with water and allowing fermentation to set in, lactic acid being formed and the gluten largely dissolved. The starch granules could then be easily washed free from the gluten. The residues could only be used as cattle food.

**Potato Starch.**—The potato contains from 16-22 per cent. of starch, 1.5 per cent. of sugar and dextrine, and 76 per cent. of water. (See p. 178, Table.)

In Germany very large amounts of starch are obtained from potatoes; 3 per cent. of the total potato production going for the manufacture of starch, 6 per cent. being utilised for industrial alcohol and spirits, the rest being consumed as food.



In Germany the potatoes are usually worked for starch in small factories situated in country districts, which usually work only in the winter months and employ the waste from the manufacture directly as cattle food.

The potatoes, when kept, lose considerably in weight through internal breathing and loss of water by evaporation. Consequently, in order to diminish loss, they are stored after harvesting in dark, cool cellars. If allowed to freeze they become sweet owing to the accumulation of sugar in consequence of the cessation of breathing (which consumes the sugar, evolving it as  $\text{CO}_2$ ). When germinating in spring a large amount of starch is lost (see under Malt), being used as food for the growing plant. The germ contains the poisonous alkaloid **Solanin**. Potatoes are invariably worked for starch during the winter months.

The percentage of starch in the potatoes is usually estimated by taking their specific gravity by means of Reimann's potato balance, the potatoes being weighed in air and in water. If  $W_a$  = weight in air, and  $W_w$  = weight in water, then their specific gravity  $S$  is given by  $S = \frac{W_a}{(W_a - W_w)}$ .

Direct experiments have shown that there is a connection between the specific gravity and the starch contents. The following figures are taken from *Behrend & Morgen's Table*:—

Specific Gravity of Potato.	Starch.	Specific Gravity of Potato.	Starch.
	Per Cent.		Per Cent.
1.080	13.9	1.120	22.5
1.090	16.0	1.140	26.7
1.100	18.2	1.159	30.6
1.110	20.3		

Young or diseased potatoes are unsuitable for starch manufacture, the former containing small undeveloped starch granules, and the latter having the granules partially destroyed, which renders the isolation of pure starch difficult.

The larger the starch granules in a potato the better the yield and quality of the prima starch.

Attempts have been made in Germany to increase the starch content of potatoes by selective cultivation, much in the same way that the enrichment in sugar of the sugar-beet has been effected (see **Sugar**, p. 144), but up to the present, however, with little success.

**Manufacture.**—The potatoes are first washed in special machines, and then cut up into a fine pasty mash by special cutting machines. The starch is washed out of the pasty mash by water. The residual fibrous matter, consisting principally of cellulose, is used for feeding cattle, and sometimes for making glucose. A brush extracting machine is used for washing out and removing the starch granules from the potato mash, the starch being obtained as a milky suspension in water. The brushes are arranged spirally round the axis of the machine, and cause the potato pulp to traverse it from end to end, subjected meanwhile to the washing effect of water. The cellulose fibres are separated by sieves, and the milky starch suspension is run either through troughs inclined at a very small angle, or into large cemented tanks. The starch sinks to the bottom and is collected, washed again in tanks with pure water, allowed to settle, and the upper layer of starch, which is impure and greyish in colour, is scraped off. By repetition a perfectly pure moist starch is obtained, containing 50 per cent. of water. The starch is now dried. In the process it must not at first be heated beyond  $40^\circ \text{C}$ ., or it begins to swell up and gelatinise. The introduction of centrifugal machines for drying has been attended with beneficial results, the centrifugal drums being provided with fine cloth, which allows the water to pass through, but not the starch. The starch is centrifuged until it contains 30-35 per cent. of water. It is then transferred to special basketwork frames or drying apparatus, and dried in warm air at  $30^\circ \text{C}$ . until it contains 17-20 per cent. of water. It is not dried beyond this, because if this were done the dried



starch on exposure to ordinary air would again rapidly absorb moisture until this percentage is attained. Potato starch is the cheapest kind of starch, being only half the price of the best rice or wheat starch.

From 80-90 per cent. of the starch in the potato can be isolated by careful work, and it comes into the market in a ground condition as a fine white powder called "Potato Flour."

Two qualities are usually sold, namely, **Prima Potato Flour**, snow white, with only a trace of nitrogen, fat, and ash (less than 0.5 per cent.), and **Secondary Potato Flour**, which is grey in colour, and contains a certain amount of nitrogenous bodies, fats, etc.

Potato starch is sometimes put on the market in a *granular form* ("**Artificial Sago**"), by mixing the damp starch with a little dextrine solution, rubbing the mass through sieves with 3-5 mm. mesh, rounding the particles in a rotating drum about 15 ft. long, dusting with powdered starch, sieving and drying at 100° C. in a chamber until a glaze is formed, then drying at a lower temperature. It is often sold as "sago" and has the same nutritive value as true sago.

The pulp left behind after the extraction of the starch amounts to about 20 per cent. of the original weight of the potato, and contains 10-20 per cent. of the total amount of starch originally in the potato, as well as much cellulose fibre, nitrogenous matter, and ash. It is either dried to 70 per cent. water and used as provender for cattle, in a fresh condition, or dried further, mixed with oil cakes, compressed, and sold in the form of cakes for cattle. The juice and liquor from the potatoes is rich in nitrogen, potassium, and phosphorus, and is used for manuring land. Potatoes contain 0.25 per cent. N, 0.2 per cent.  $P_2O_5$ , and 0.6 per cent.  $K_2O$ . (See Table, p. 177.)

**Manufacture of White Potato Starch in America by the Batch and Continuous Processes.**—To meet the increased demand for white potato starch in America and to replace the starches imported before the 1939 War, the potato starch production of America has recently been enormously increased. In addition to increasing the productive capacity in Maine, the potato starch industry has been established in Idaho since 1941, raising the nation's productive capacity to 100,000,000 lbs. per year.

Cull and surplus potatoes are used from crops grown near the factories. The continuous process is largely used by the more modern factories, the older ones employing the batch process.

**The Batch Process.**—Washed potatoes are fed to a grater-surfaced drum which grinds them to a slurry, which is screened through a 90-mesh shaker screen by means of water sprays. The starch milk passing through the screen is run into a settling tank, and the pulp is reground by means of a hammer mill and rewashed on the screen, the washings passing into the vat containing the first washings. The pulp from the second screening is now thrown away, although some countries, *e.g.*, Germany before the War, used these in the manufacture of cattle cake.

The starch is allowed to settle in the vat overnight, and then the protein water (the supernatant liquid above the starch in the vat) is run away (to waste). The starch is then resuspended in fresh water which, in due course, is also drained away. The remaining starch settles roughly into two layers—brown starch containing fine fibres which settled last, and white starch at the bottom. The brown starch is then slurried and pumped into a small vat, where the white starch it contains is separated on the bottom. The white starch from the large vat is then pumped into a centrifugal feed vat. The brown starch layer from the small vat then passes into the sewer, and the white starch from this vat then passes into the centrifugal feed vat with the main batch of white starch, whence the white starch in slurry form is passed, as required, to the centrifugal dewaterer. Hot-air drying to 16 per cent. moisture and pulverising then completes the process.

**The Continuous Process.**—This process produces partially refined starch in less than ten minutes after the grinding of the potatoes. Finished starch requires about five hours.

The process runs as follows: After tumbling in a concrete trough to wash the potatoes, they are led to a hopper which feeds a potato rasp. The ground potatoes drop into a pit containing water treated with sulphur dioxide. The



slurry is then pumped to an extractor set, comprising a bottom shaker screen, bottom rotary brush sieve, top shaker screen, and top rotary brush sieve. (For a detailed account see "Industrial and Engineering Chemistry" (August 1948), p. 1405.) The starch milk from the bottom shaker screen of the extractor set then passes to a continuous centrifugal separator which removes most of the protein (in water). The starch is then diluted and passed through a 120-mesh refining screen which removes the remaining fine fibre. From this screen the starch is pumped to two sets of settling tables. The liquid is run off into the sewer and the settled starch slurried with water and run into storage tanks. As required, the starch is then passed to a continuous rotary vacuum filter which reduced the water content of the starch to 40 per cent. (a cake). These cakes are then delivered to a belt drier (hot air) which reduces the moisture content to 16 per cent.

**Comparison of the two processes.**—Owing to the fact that less starch is lost in separating the fine fibre from the starch by screening, followed by tabling, rather than by separating the brown starch in vats, the continuous process is found to give a higher yield. The waste materials from the continuous process contain 24 per cent. starch and 32 per cent. protein, while those from the batch process contain 45 per cent. starch and 28 per cent. protein.

On the continent of Europe the waste materials are fed to livestock, but in America this is not generally done.

**Maize Starch or Corn Starch Manufacture**, now an enormous industry in the United States, is carried out by steeping maize in large hopper-bottomed wooden vats with water containing 0.3–1 per cent. of sulphur dioxide,  $\text{SO}_2$ . The steeping lasts two to four days, the hot  $\text{SO}_2$  water being kept in circulation by steam siphons and heat is supplied to maintain the temperature at  $40^\circ$ – $50^\circ$  C. ( $120^\circ$ – $140^\circ$  F.).

The steep water is either run to waste or evaporated to recover the soluble extract as cattle food.

The disintegrated grain is crushed in a Foos mill and stirred up with water. There remains a sediment of unground maize (which is reground) while the finely ground portions pass away suspended in water through a large V-shaped tank (the "Degerminator") fitted with a screw conveyer in the bottom and skimming paddles at the top. The **germ** of the maize floats and is skimmed off by the paddles and so separated.

The separated germ is washed free from starch, cooked with live steam, and "**maize-oil**" or "**corn-oil**" is manufactured by pressing, the solid residue being sold as a cattle food, as "**oil-cake**" or "**maize-germ cake**." See p. 44.

The endosperm, starchy and dextrinous matter, bran, fibres, etc., pass on in the liquors, known as **separator-liquors**. These liquors are first of all passed over vibrating copper sieves, which retain the coarser particles, bran, fibre, etc., the starch suspension passing on to other sieves.

The coarse material retained by the copper sieve at this stage is caught in elevators, conveyed afresh to the grinding mills, ground with water in burr-stone mills, pumped to mechanically stirred feed vats, and the liquor coming from these is united with the above mentioned "separator liquors" coming from the degerminator.

The starch-containing liquors coming from the copper sieve now pass over a series of sieves known as "shakers," being made of No. 10 bolting cloth stretched over wooden frames. These receive a vibratory motion from an eccentric shaft, the shakers being set on hickory sprains to give a rapid but soft motion. The starch cells pass through as a milky liquor, while a mass of grain and bran is left behind on the sieves ("shakers").

This residue is stirred with water to wash out starch, then pressed and sold as "**press feed**"; or it is dried and sold as "**corn bran**." It contains: Proteids, 10.5 per cent.; fat, 2.75; carbohydrates, 65.0.

The milky liquor running through the sieves is known as "mill liquor" or "crude starch liquor." It contains the starch as a fine suspension, 1 gal. containing



5.4 oz. pure starch and 1.5 oz. of "dry feed." Its specific gravity is 3° Bé. It is (sometimes) run through another series of sieves (to remove fibres, etc.) and then is made to flow over a long series of wooden gutters (usually made in sixteen sections, each 120 ft. long and 6-7 in. deep, and each section divided by wooden partitions into three channels each 18 in. wide and having a slope of  $\frac{3}{8}$  in. in every 12 ft.). The speed is 1 gal. per thirty-five secs., the entering density of the liquor being 3.5° Bé. The starch granules are here almost completely deposited, the out-flowing liquid only possessing the specific gravity of 0.5 Bé. and escaping at the rate of 1 gal. per twenty secs.

The escaping liquors are either run into settling tanks, settled, and the supernatant clear liquid siphoned off and the fluid mass underneath sold as a cattle food ("swill" or "slop").

Sometimes the sediment is pressed and sold as "gluten-meal."

The starch which has deposited in the gutters or runs is now shovelled out. It contains 50 per cent. water and is impure. It is made into a paste of 7° Bé. with water in large wooden vats ("breakers") provided with stirring gear, and a solution of caustic soda of 3° Bé. run in until the liquid turns greenish yellow. The alkali neutralises acidity, precipitates some proteid, emulsifies or dissolves any oil.

The fluid is now diluted to 3.5° Bé. in vats, and once more sent down the separating gutters. The starch separated this second time is once more mixed with water, run into shallow pine-wood draining boxes, provided with perforated bottoms. The moisture drains off overnight and the blocks of moist starch (55 per cent.  $H_2O$ ) are then dumped out of the boxes on to the drying floors.

Very often the starch after coming from the gutters after the alkali treatment is further purified by mixing with water to 11°-12° Bé., and is then placed on a series of sieves or shakes, where any coagulated material separates, the starchy fluid pouring through at 8° Bé. This liquid is then settled, the supernatant liquid run off, fresh water added, and the mass, of sp. gr. 24° Bé., is run into the draining boxes as above described. Sometimes the alkali treatment is omitted, this "un-chemicalled starch" being used for baking powder, or as size in the textile industries.

The drying of the starch is best done in vacuum. The purified starch paste is first run into boxes lined with linen, and placed in a vacuum chamber. Rapid drying takes place in a few hours. The starch in these boxes is cut into 7-in. cubes, placed in a hot air drying chamber provided with an exit for moist air. In the stream of dry air the starch completely dries in a few hours.

In the old system of drying (still used), the starch was first dumped on to drying floors made of porous brick, covered with plaster of paris, and heated by steam pipes from beneath. Here the moisture content is reduced from 55 per cent. to 45 per cent. The starch is now crushed, placed in small blocks on shelves in a hot air drying kiln, and dried at 120°-130° F.

The yellowish crust which forms on the outside is scraped off, and the blocks redried at 156°-176° F. for three to sixteen days. The scrapings are worked for starch, using alkali as before.

Maize yields 59 per cent. of starch, decorticated maize giving 68 per cent.

Maize starch is put on the market as (1) **Thin boiling starch** prepared by suspending **unchemicalled starch** in water (22° Bé.), adding hydrochloric acid to the water in the mills, then boxing and draining and drying the starch as described above. The HCl converts some of the starch to a soluble form, whereby it yields a paste of low viscosity. This is the "drying-in" process. In another process, called the "in-suspension" process, the suspension of starch in water (22° Bé.) is heated to a temperature well below the gelatinisation temperature with a little HCl or  $H_2SO_4$ , with continual stirring. The starch is then run into boxes and dried.

The thin boiling starches are used in laundry and confectionery work, and produce a thin paste.

(2) **Thick boiling starch** is the ordinary starch, dried slowly as above described. When very thick boiling starches are wanted, either for use in baking powder or as size in the textile industries, the treatment with alkali (see above) is omitted, the starch being merely run through the gutters or runs a second time and dried slowly. The protein is thus not removed, and so the material has a greater "agglutinating" power.

The starches "**Mondamin**" and "**Maizena**" are prepared from maize.



**Cornflour** is made from maize or Indian corn, large factories existing at Paisley in Scotland, the process of manufacture being very similar to that above described. Rice starch, similarly treated, is sold for dietetic purposes as "British Cornflour," etc.

**Manufacture of Arrowroot.** — The roots of the plant *Maranta arundinacea* are collected, thoroughly washed, and the skin removed with suitable knives. The skin, if left on, discolours the starch and imparts to it an unpleasant flavour (owing to resins contained therein). After removal of the skin the roots are washed, pulped by crushing between copper rollers, or by pressing against water, and the pulp is transferred to upper cylinders provided with small perforators, where it is thoroughly agitated and treated with a current of water.

The starch is thus separated from fibre, etc., and is carried away in the milky liquid issuing from the cylinders, the woody matter, etc., remaining behind. The liquid is now filtered through fine muslin sieves (to separate any floating fibre) and is then allowed to settle in reservoirs, when it is washed with fresh portions of clean water after each settling. The starch is then transferred to shallow copper pans, covered with fine white gauze (to protect from dust, etc.), and allowed to dry. When dry it is packed in small barrels for shipment.

The composition of the roots is given by Leuscher (*Journ. Chem. Soc.*, 1902), as:  $H_2O$  = 63.4 per cent.; starch = 27.8 per cent.; dextrin and sugar = 2.08 per cent.; fibre = 3.9 per cent.; ether extract = 0.19 per cent.; proteid = 1.64 per cent.; ash = 0.89 per cent. **Arrowroot starch** contains: starch, 83.7 per cent.;  $H_2O$ , 15.9 per cent.; fibre, 0.04 per cent.; sugar, gum, 0.18 per cent.; ash, 0.14 per cent.; proteid, 0.0.

**Tapioca** is prepared from the *Cassava* or *Mandioc* plant of South America. The tubers are washed, peeled, pounded to pulp, pressed in baskets to expel the poisonous juice, and the meal thus obtained is sifted (to remove fibre), dried by gentle heat (never sufficient to colour the meal), which expels the last traces of the poisonous juice. **Cassava starch** is prepared by repeatedly washing the fine meal with water, the sediment allowed to settle, the water decanted, and the starch is sun-dried. **Tapioca** is made from the moist starch by heating on metal plates. The starch grains swell, burst, and become agglutinated into the commercial granular "tapioca."

**Manufacture of other Varieties of Starch.** — Starch is also manufactured from various other tropical plants, e.g., Curcuma, Tacca, and Sago. Sago starch is obtained by kneading with water the pithy interior of the sago-palm. "**Pearl sago**" is obtained by forcing the moist sago starch through sieves, rolling in cloth, and heating with a little fat in pans. Pearl sago contains: starch, 84.6 per cent.;  $H_2O$ , 15.2 per cent.; ash, 0.11 per cent. Large amounts come from Singapore. A similar granular substance made from starch meal is known as "**Artificial Sago**" (see under Potato Starch).

**Soluble Starch** is obtained by boiling starch with water, the solution being rendered quite clear by the addition of a little caustic alkali. If starch paste is heated to boiling under 2-3 atmospheres pressure a strongly dextro-rotatory solution ( $[\alpha]_D = +198^\circ$ ) is obtained, which gives a deep blue colour with iodine; the addition of alcohol causes the precipitation of the "soluble starch" as a white powder, which, however, will not again completely dissolve in cold water.

Other ways of rendering starch soluble are: stirring starch powder with a solution of caustic soda, also by stirring with water and warming with malt (diastatic action), dil.  $H_2SO_4$ , or bleaching powder.

A recent patent (German Patent, 134,301) describes the manufacture of a soluble starch by mixing 100 kg. of starch flour with 3.5 kg. of ammonium persulphate and 150 l. of cold water, standing for ten hours, filtering and washing until free from persulphate, and drying. The nascent O from the persulphate  $[(NH_4)_2S_2O_8 + H_2O = 2(NH_4).HSO_4 + O]$  acts on the starch and renders it soluble.



The product dissolves in hot water to a clear solution which solidifies on cooling to a jelly. Used in dressing textiles.

Boiling with a volatile organic acid (formic or acetic, German Patents, 182,558 and 137,330) also renders starch soluble. The acid may be easily distilled off, and neutralisation is unnecessary.

Starch is also rendered soluble by treating it with Cl gas and then heating to 100° (German Patents, 149,588 and 168,980), by treating with  $\text{KMnO}_4$  (German Patent, 156,148), by heating powdered starch to 62°-63° C. with HCl vapour (American Patent, 773,469), etc., etc. **Ozone** renders starch soluble.

A starch which has the power of swelling up with cold water is made (German Patent, 157,896) by stirring between 10°-30° C. with 50-80 per cent. of methyl or ethyl alcohol, so as to make a thin milky liquid suspension of starch. To 100 parts of the mixture 40 parts of caustic soda solution (30° Bé.) are added, and then after some hours' standing, acetic acid. The starch is pressed out of the wet alcoholic solution, dried and ground. Useful for dressing textiles and for manufacturing adhesives.

A similar starch is made by stirring starch with warm  $\text{Na}_2\text{SO}_4$  solution, adding  $\text{NaOH} + \text{Na}_2\text{SO}_4$  solution, standing for ten minutes, pressing, drying and powdering (German Patent, 166,259). See also **Dextrine**.

**Bleaching Starch.**—The practice of bleaching flour and starch has been declared by some authorities to be a highly deleterious one, while others assert that the custom is harmless. The process is carried out by exposing the starch or flour to the vapours of **Nitrogen Peroxide**. The nature of this material suggests that it is undesirable. Other peroxides are sometimes used.

**Uses of Starch.**—Besides being used as a food, starch is used in the arts for a variety of purposes, most of these depending upon its capacity for gelatinising with water and forming a paste. Starch is used:—

1. In laundry work for stiffening linen collars, shirts, etc. The gelatinised starch is applied in a thin layer over the article, and is converted by the passage of a hot iron into a shiny stiff layer of **dextrine** (which see). The **starch glazes** are made by adding borax, finely powdered stearic acid, or paraffin to potato starch, and give a shining silvery lustre. Potato starch is the cheapest variety of starch, and so is largely used for this purpose. Wheat starch or, still better, rice starch (which can be used with cold water, thus avoiding the trouble of boiling with water necessary with potato starch) are superior to potato starch for laundry purposes, but are dearer. By mixing starch with azo-dyes coloured starches can be obtained, which wash white again.

2. As an adhesive, much is used by the paperhanger, bookbinder, etc. Potato starch forms a poor adhesive; wheat or maize starch are much superior for this purpose. "**Gloy**" is said to be a mixture of dextrine and starch with magnesium chloride (see **Dextrine**).

3. Many mixtures of starch and dextrine are employed as thickening agents for colours and mordants in calico printing, etc. etc. The pastes must be free from acid and alkali.

4. For sizing paper, a mixture of starch paste and rosin is used.

5. Thin starch pastes are largely used for finishing and weighting calicoes, lace curtains, and cloths. Such pastes must be thin, and wheat starch is the best for the purpose, since it sinks into the fabric more thoroughly than potato or maize starch. The cloth is, after soaking in the paste, passed through hot rollers, and so finished with a fine glaze.

6. Fine rice starch is used as a face powder. Fine starch is also used for dusting moulds in metal founding.

7. As a thickening agent for sauces, puddings, etc. etc.

8. Large quantities of starch are worked up into dextrine (or British gum), brewing and preserving sugars or dextrose, glucose, burnt sugar or caramel for colouring beer, etc. etc.

9. In a non-isolated condition the starch of potatoes and grain serve as a food (bread, etc.), and as the source of alcohol in beer and spirits, all of which are manufactured from starchy material.

**Estimation of Starch, Testing Starch.**—The amount of starch in grain and potatoes is determined by hydrolysing the starch completely into dextrose with very dilute  $\text{HCl}$ . The starch-containing material in a finely divided condition is first heated in an autoclave at 3 atmospheres with water, or diastase is added. The starch is thus dissolved in the water, the cellulose and fibres remaining behind and are separated by filtration. The clear filtered starch solution is now converted into dextrose (by heating with dil.  $\text{HCl}$ ), which is estimated in the usual way with Fehling's solution. 100 parts of dextrose are obtained from 92-93 parts of starch (theory=90).

Qualitatively the presence of starch may be detected by the blue colour it gives with iodine.

A microscopic examination (see p. 176) determines the nature of the starch (rice, potato, wheat, etc.) and whether adulterated. Good starch should not contain more than 20 per cent. water, which is estimated by heating 10 g. starch to 40°-50° C. (not higher) for one hour, then to 120° C. for four hours, cooling in desiccator, and weighing.



Acids, if present in the starch, are estimated (Saare) by stirring 25 g. starch with 30 c.c.  $H_2O$  to form a thick paste, and titrating the paste with  $\frac{N}{10}$   $NaOH$  until a drop of the solution placed on a folded filter paper is not coloured red with litmus; a control experiment is necessary, using neutral starch. 100 g. of a *slightly acid* starch require 5 c.c.  $\frac{N}{10}$   $NaOH$ . The starch is *acid* if it requires 8 c.c.  $\frac{N}{10}$   $NaOH$ , and *strongly acid* if more than 8 c.c. are required for neutralisation.

The adhesive power of the starch is determined (Scheil) by mixing 4 g. with 50 c.c. water, and boiling over a Bunsen burner until the paste is transparent and begins to froth. The burner is removed and paste well stirred. The heating must not last for more than one minute. 4 g. in 50 c.c. of  $H_2O$  of a normal starch sets, on cooling, to a paste which cannot be poured out of the dish.

Impurities may be estimated in the ash of the starch, or in the residues left after dissolving out the starch. Starch is easily brought into solution by warming at  $65^\circ C.$  for two hours with a normal malt solution (100 g. malt in 1 litre water).

## DEXTRINE, BRITISH GUM, STARCH GUM

When starch is heated to  $180^\circ$ - $200^\circ C.$  for a short time, or when moist starch paste is heated with a trace of acid, best with  $HCl$  or some other easily volatile acid, it is converted into a thick gum-like mass, possessing powerful adhesive properties, and which is in consequence largely used as a substitute for the expensive gum-arabic.

Dextrine is not such a powerful adhesive as gum-arabic, and papers covered with it easily become moist in wet weather, but it is far less expensive, and consequently is much used as the gum for paper labels, stamps, envelopes, etc. It has the advantage over starch as an adhesive that it dissolves in cold water and need not be boiled. Mixtures of dextrine and starch paste are on the market as adhesives ("Gloy" is said to be such a mixture with magnesium chloride) and as a thickening agent in colour printing.

Dextrine is prepared from starch in two ways:—

1. **The Acid Process.**—This is steadily gaining ground; it consists in taking the damp "green" starch, fresh from sedimentation, and mixing with it 0.2-0.4 per cent. of concentrated hydrochloric or nitric acid and heating in open pans in a closed chamber heated to  $150^\circ C.$  The acids volatilise and the dextrine is left as a yellowish glassy mass, which usually contains a small amount of starchy matter insoluble in water, and a small percentage of dextrose.

2. **The Roasting Process.**—The starch is heated without acids in rotating cylinders to a temperature of  $180^\circ$ - $200^\circ C.$ , the starch being fed in at one end and removed as dextrine at the other. In Lehmann's process the starch is placed in closed vessels provided with powerful stirring apparatus and heated at the bottom by superheated steam to the necessary temperature. It yields a better product than the rotating cylinder method.

"Crystallised British gum," "crystallised gum," etc., is simply dextrine which has been decolourised with animal charcoal and evaporated down until on cooling it gives a light coloured brittle mass, similar to dried gum-arabic.

**Statistics.**—In 1910, about 92,000 cwt. of dextrine, of value £63,000, were imported into England, and 3,800 cwt., of value £3,200, were exported. The United States in 1910 imported 6,392,000 lbs. (value \$197,000).

For modern statistics see Appendix III.

**Shoemakers' Paste** (see p. 180) is also a dextrine. See also under **Glue, Gums.**

For the manufacture of **Starch Syrups**, starch sugar, glucose or dextrose, see under **Glucose.**



## BAKING POWDERS

By GEOFFREY MARTIN, D.Sc., Ph.D., F.I.C.

**Baking Powders** may be defined as any powders used as a substitute for yeast in making bread or pastry.

Yeast acts by evolving carbon dioxide gas, which renders the bread spongy, the gas being liberated as a result of the vital processes of the yeast cell.

Baking powders also act by evolving carbon dioxide, but this is liberated by the chemical action of an acid on a carbonate.

**Composition.**—The best baking powders are made from a mixture of tartaric acid, cream of tartar, and sodium bicarbonate, together with a diluent such as starch or flour.

The following is a typical baking powder of this type:—

Tartaric acid	-	-	-	-	6.25 per cent.
Cream of tartar	-	-	-	-	18.75 „
Sodium bicarbonate	-	-	-	-	25.00 „
Rice flour	-	-	-	-	50.00 „

It is a great advantage for the carbon dioxide to be liberated slowly, because a dough can then be kept some time before baking. This is achieved by adding cream of tartar to the baking powder, because it is only slightly soluble in cold water, but readily soluble in hot, whereas tartaric acid is readily soluble both in cold and hot water. Hence, when mixed cold into the dough the moisture causes the evolution of a certain amount of gas by the action of the free tartaric acid on the carbonate. When the dough begins to be baked, and becomes hot, a second slow evolution of gas occurs owing to the cream of tartar now dissolving in the hot water present, and acting further on the sodium bicarbonate. Also this mixture of substances does not darken the bread.

The addition of tartaric acid is not essential; e.g., Crampton's powder contains:—

Cream of tartar	-	-	-	-	50 per cent.
Sodium bicarbonate	-	-	-	-	25 „
Maize starch	-	-	-	-	25 „
					100

Very often, however, the cream of tartar is left out as in the following typical baking powders. Also the sodium bicarbonate is sometimes replaced by sodium carbonate or magnesium carbonate, and occasionally (for very light pastries) by ammonium carbonate:—

	1.	2.	3.	4.	5.	6.
<i>Tartaric acid</i>	65	28	25	25	17.5	10
<i>Sodium bicarbonate</i>	25	32	25	25	...	10
<i>Sodium carbonate</i>	...	...	...	...	27.5	...
<i>Magnesium carbonate</i>	...	12	...	...	...	...
<i>Farina (potato flour)</i>	15	28	...	...	55.0	...
<i>Rice flour</i>	...	...	50	...	...	80
<i>Maize starch</i>	...	...	...	50	...	...

In many baking powders the tartaric acid is replaced by acid salts, such as **acid ammonium phosphate**, **acid potassium** and **calcium phosphates**, and **acid potassium sulphate**. These substances, however, tend to darken the bread.

Examples of such baking powders are :—

1. Acid calcium phosphate	-	-	10	2. Acid sodium phosphate	-	-	20
Cream of tartar	-	-	25	Acid calcium	-	-	20
Sodium bicarbonate	-	-	25	Sodium bicarbonate	-	-	25
Corn flour	-	-	40	Starch	-	-	35
			<hr/> 100				<hr/> 100
3. Acid potassium sulphate	-	-	60				
Sodium bicarbonate	-	-	20				
Corn flour	-	-	20				
			<hr/> 100				

**Horsford's Powder** consists of two packets : (1) acid calcium phosphate and acid magnesium phosphate mixed with flour ; (2) sodium bicarbonate, with a little potassium chloride.

Occasionally the **starchy dilute** is replaced by **powdered milk**, which is stated (Hooker) to have a better leavening power and be more nutritious.

54 parts milk powder, 20 parts tartaric acid, and 1 part water are recommended. See *Journ. Soc. Chem. Ind.*, 1908, Vol. 27.

**Self-Raising Flours** are simply flours ready mixed with baking powder for use.

One well-known brand consists of  $\frac{1}{2}$  lb. sodium bicarbonate and  $1\frac{1}{2}$  lbs. cream of tartar, mixed with 112 lbs. flour

Sometimes a little tartaric acid is added.

**Manufacture of Baking Powders.**—The materials are thoroughly dried, then mixed in special mixers, and the whole then passed through a fine sieve, and kept in air-tight packages in a dry place.

The presence of moisture causes the acid to act on the carbonate, and thus causes the powder to deteriorate. So long as the powder is kept perfectly dry no marked action can take place.

**Analysis of Baking Powders.**—Baking powders should be tested for alum and other injurious ingredients which render discoloured flour white, but indigestible. Arsenic, lead, etc., are also to be looked for. The amount of carbon dioxide evolved by action of acid, or on heating, may also be estimated in order to see whether the powder has deteriorated. A baking powder should evolve at least twenty times its volume of carbon dioxide.



## SECTION IV

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### The Cellulose Industry





# THE CELLULOSE INDUSTRY

BY A. J. CARRIER, B.Sc., AND G. MARTIN, Ph.D., D.Sc.

## I.—CELLULOSE, $(C_6H_{10}O_5)_n$

### LITERATURE

See also under "Paper-Making," "Celluloid," "Artificial Silk."

- Article on "Cellulose" (Dr Frankland Armstrong) in Allen's "Commercial Organic Analysis," vol. i., 1909, third edition, where analytical methods are discussed.
- J. BERSCH (Translated by W. T. BRANNT).—"Cellulose, Cellulose Products, and Artificial Rubber." Philadelphia and London, 1904.
- CROSS AND BEVAN.—"Researches on Cellulose." 1895-1900, 1900-1905. London.
- " " "Cellulose." London, 1895.
- " " "Wood Pulp." London, 1911.
- SCHWALBE.—"Chemie der Cellulose."
- C. PIEST.—"Die Zellulose." Stuttgart, 1910.
- MAX SCHUBERT.—"Die Cellulosefabrikation." Berlin, 1906.
- B. M. MARGOSCHES.—"Über die Viscose." Leipzig-Gohlis, 1906.
- MAX SCHUBERT.—"Die Holzstoff oder Holzschiff-Fabrikation." 2nd Edition. Berlin, 1909.
- O. DAMMER.—"Chemische Technologie der Neuzeit." Articles on "Cellulose," "Celluloid," "Artificial Silk," etc. Stuttgart, 1911.
- E. C. WORDEN.—"Nitrocellulose Industry." 2 vols. London, 1911.

CELLULOSE forms the basis of the solid framework of plants, and is the most widely-distributed carbohydrate of the vegetable kingdom. It occurs nearly pure in cotton, linen, and in the pith of many plants. Cellulose forms the raw product for the manufacture of paper, nitro-cellulose (gun-cotton), celluloid, artificial silk, and similar products.

Cellulose is obtained very largely from wood, grasses, and, in small part, from straw. Among plants which are largely cultivated as sources for cellulose may be mentioned cotton, flax, hemp, jute, esparto, China grass or ramie, etc.

The formula for cellulose is  $(C_6H_{10}O_5)_n$ . The molecular weight is unknown, but is undoubtedly very high.

Cellulose is more stable than starch. When air-dried, it contains 6-12 per cent. of water, which is driven off at  $100^\circ C.$ , but is re-absorbed on exposure to air. Several cellulose hydrates exist, which give an indigo-blue coloration with iodine in aqueous solution. Treated with dil.  $HNO_3$  or chromic acid, cellulose is oxidised to an oxycellulose; concentrated  $HNO_3$ , however, nitrates it. (See **Collodion**). Prolonged boiling with dilute acids converts cellulose into hydrocellulose,  $(C_6H_{10}O_5)_n \cdot H_2O$ , which is distinguished from cellulose by containing free carbonyl groups, and the greater reactivity of its OH groups.

The acetyl compound,  $C_{12}H_{14}O_4(O.CO.CH_3)_6$ , an amorphous mass soluble in  $CHCl_3$ , is produced by heating cellulose with acetic anhydride to  $180^\circ C.$

Concentrated sulphuric acid causes cellulose to swell up and dissolve to a paste-like compound called amyloid, which is precipitated by water. If the solution be greatly diluted and heated to  $120^\circ C.$ , an almost quantitative yield of dextrose is produced. This when fermented yields alcohol—one of the suggested methods of obtaining alcohol from wood.

The enormous magnitude of the cellulose industry (including wood and timber, paper, wood fibre, celluloid, etc.), may be gauged from the following statistics:—

## IMPORTED INTO THE UNITED KINGDOM.

	1906.	1910.	Value in 1910.
Wood and timber - - - - -	10,080,000 loads	9,820,000 loads	£24,350,000
Furniture woods, hard woods - - - - -	279,000 tons	270,000 tons	1,870,000
Manufactured wood - - - - -	...	...	2,340,000
Paper - - - - -	452,000 tons	548,000 tons	6,410,000
Paper-making materials - - - - -	834,000 „	1,085,000 „	4,970,000
Celluloid ware - - - - -	...	...	450,000
Artificial silk - - - - -	...	...	40,000
Total value - - - - -	...	...	£40,430,000

## EXPORTED FROM THE UNITED KINGDOM.

	1906.	1910.	Value in 1910.
Wood, timber, and manufactured wood -	...	...	£1,960,000
Paper - - - - -	71,000 tons	144,000 tons	3,120,000
Paper-making materials - - - - -	112,957 „	165,217 „	744,000
Xylonite and celluloid ware - - - - -	...	...	167,000
Artificial silk - - - - -	...	...	196,000
Total value - - - - -	...	...	£6,187,000

The magnitude of the United States cellulose industry is shown by the following figures :—

	IMPORT, 1910.	EXPORT, 1910.
Wood, and manufactures of - - - - -	\$54,422,000	} \$78,814,000
„ unmanufactured - - - - -	51,221,000	
Paper, and manufactures of - - - - -	17,536,000	
		16,083,000

For *details*, see under special articles. For linen, cotton, jute, etc., see under **Textile Fibres**.  
For modern statistics see Appendix III.

## Estimation and Valuation of Cellulose

1. The percentage of cellulose in a sample is best determined by Cross and Bevan's chlorination process (*Trans. Chem. Soc.*, 1889, 55, 199). 5 g. of the fibre dried at 100° are boiled for half an hour with 1 per cent. NaOH, washed and squeezed to remove NaOH and water, placed in a beaker and subjected to a slow stream of chlorine. The non-cellulose portions (lignin, etc.) form soluble chlorinated products. After thirty to sixty minutes' exposure the product is washed, heated to boiling with a 2 per cent. sodium sulphite solution, 0.2 per cent. NaOH added, boiled for five minutes, filtered, washed, and dried at 100° C. For other methods see Allen's "Commercial Analysis," vol. iii. (1909 ed.).

2. The "copper" value is determined by boiling 3 g. of the cellulose with 200 c.c. H<sub>2</sub>O and 100 c.c. Fehling's solution. The weight of metallic copper calculated on 100 parts of dry cellulose represents the copper value. Hydrocellulose gives 2 to 8.8, oxycelluloses give 7.6 to 35. The copper value gives the number of free carbonyl groups in cellulose, and hence is a measure of its stability. Those sorts of maximum resistance contain no free carbonyl groups (copper value = 0). The oxycelluloses are less resistant to hydrolysis, and hence are less stable and more perishable than normal cellulose.

3. The "ash" and "moisture" in cellulose are determined by the usual chemical methods.

## Cellulose Solutions

Cellulose is insoluble in water and simple solvents. Certain metallic salts, however, cause it to combine with water, passing through the condition of gelatinous hydrates into a homogeneous viscous solution.



(a) **Zinc Chloride Solution in Water.**—1 part of cellulose is digested in a solution of 4-6 parts  $\text{ZnCl}_2$  in 6-10 parts water, at a temperature of  $60^\circ$ - $100^\circ$  C. A homogeneous syrup results, which is employed for making lamp filaments by squirting through a fine orifice into water or alcohol. The precipitated hydrated cellulose-zinc-oxide is treated with dil.  $\text{HCl}$  and well washed.

**Vulcanised Fibre** for making valve discs, etc., is made by treating sheets of paper with  $\text{ZnCl}_2$  solution, and subjecting the gelatinised sheet to pressure (see under **Paper**).

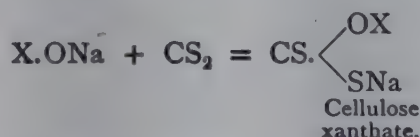
Zinc chloride dissolved in  $\text{HCl}$  (40 per cent.) dissolves cellulose in the cold, but on keeping the solution hydrolyses.

(b) **A Solution of Cuprous Hydroxide in Concentrated Ammonia** (cuprammonium solution) gradually gelatinises and dissolves cellulose. The cellulose may be recovered unchanged as a white flocculent precipitate by acidifying with dil.  $\text{HCl}$  or  $\text{H}_2\text{SO}_4$ .

This property is used in the manufacture of "Willesden" fabrics. Vegetable textiles are passed through a bath of cuprammonium hydroxide, and thus are coated with a film of gelatinised cellulose containing copper oxide, hence the well-known green colour (see under **Paper**).

(c) **Viscose or Cellulose Thiocarbonate or Xanthate Solution.**—Bleached cotton, etc., is treated with excess of a 15 per cent. solution of  $\text{NaOH}$ , squeezed until it retains three times its weight of solution. The soda cellulose obtained is treated in a closed revolving barrel at a temperature of about  $15^\circ$  C., with  $\text{CS}_2$ , in quantity about 40 per cent. of the weight of the cotton. After about three hours the mass is covered with water, and allowed to stand. On stirring, a crude solution is obtained, from which pure viscose may be made by treatment with brine or with alcohol.

The above reaction may be represented by the typical equation



where X represents the cellulose residue,  $\text{C}_{12}\text{H}_{19}\text{O}_9$ , or  $\text{C}_6\text{H}_9\text{O}_4$ . The process was patented by Cross and Bevan (English Patent, No. 8,700, A.D. 1892).

Viscose is reconverted into cellulose (1) spontaneously, on long standing; (2) by heating; (3) by treatment with oxidising agents. This property is taken advantage of in the production of artificial silk or lustra-cellulose (which see), in sizes for paper pulp, for surfacing and finishing paper, and for cloth yarns, for making photographic films, and for agglomerating various filling materials, and finally, in making vehicles for paints. See also **Artificial Silk**, the **Viscose Process**.

(d) Cellulose is also dissolved by heating at  $180^\circ$  C. with 7 parts of acetic anhydride, the triacetate,  $\text{C}_6\text{H}_7(\text{C}_2\text{H}_3\text{O}_2)_3\text{O}_2$ , being produced. The cellulose acetates have now important uses. See under **Cellulose Esters**.



## II.—WOOD AND TIMBER PRESERVATION, Etc.

### LITERATURE

- B. MALENKOVIC.—“Die Holzkonservierung.” Vienna, 1906.  
 P. CHARPENTIER.—“Timber.” London, 1902.  
 NORFOLK CREOSOTING CO., U.S.A.—“Creosoted Timber.” 1909.  
 ANDES.—“Feuersicher-, Geruchlos-, und Wasserdichtmachen.” Vienna, 1896.  
 „ “Das Conserviren des Holzes.” Vienna, 1895.  
 W. B. CAMPBELL, B.Sc.—“Preservative Treatment of Wood.” *Journ. Soc. Chem. Ind.*, 1915, 34, 257.  
 CARTWRIGHT AND FINDLAY.—“Decay of Timber and its Prevention.” H.M. Stationery Office, 1946.

The chemical constitution of wood has been dealt with under **Cellulose**. For statistics regarding timber, see p. 188.

### Treatment of Timber

Timber is very liable to decay, and thus it is that all timber used for constructional engineering is specially treated.

(a) **Impregnating**.—Timber to be used for railway sleepers, telegraph poles, etc., is impregnated with antiseptic chemicals, such as creosote oil, zinc chloride, copper sulphate, etc.† The wood is dried by stacking for some months; then it is placed on iron bogie frames which are run upon rails into a very strong horizontal iron boiler (say 30-60 ft. long by 6-7 ft. in diameter), which is then closed by a cover. The air is exhausted up to  $\frac{1}{8}$  atmosphere so as to remove air from the wood pores, otherwise the air contained in them would resist the entrance of the oil. Next creosote oil\* is run in, deeply penetrating into the pores of the wood until the latter is saturated, then a force pump forces more oil into the cylinder until a pressure of 8-10 atmospheres is attained, the pressure being maintained for several hours. The wood absorbs about 1 gallon of oil per cubic foot. This creosoting process is almost exclusively used for telegraph poles, railway sleepers, and piles. Sometimes impregnation is carried out with zinc chloride solution, less often with copper sulphate solution, and now very rarely (on account of expense) with mercuric chloride. Other chemicals used are aluminium sulphate, sodium aluminate, ferrous sulphate, sulphate and borate of ammonium, sodium fluoride, etc. etc.

One of the chief difficulties of creosoting is the presence of moisture in the wood, which impedes the entrance of the oil, because oil and water will not mix. This is the reason why timber after cutting must be “stacked,” or air dried, for some months. Vohl proposes to treat green timber by adding enough caustic soda to the creosote to make it miscible with water, impregnating the timber, and “fixing” the creosote with dilute ferrous sulphate. Other attempts consist in making the oils soluble in, or emulsionable with water by sulphonation, by adding soap (0.5 per cent.), zinc chloride, etc. (See German Patents, 139,441, 152,179, 118,101, 150,100.)

The disadvantage of creosoted wood is its great inflammability and smell. Impregnation with metallic salts renders wood almost non-inflammable. Boiling wood with sugar solution for some hours, and drying on hearths, protects wood against mildew and rot, and increases its strength.

(b) **Metallisation**.—Here the wood is impregnated successively with two solutions of salt, which combine in the fibres, forming an insoluble precipitate, e.g., the wood is soaked with a soluble copper or zinc salt, and then impregnated with a solution of a resin salt. Insoluble copper or zinc resins are deposited in the fibres. Similar solutions are: Calcium chloride followed by water glass (Na silicate); calcium chloride +  $\text{Na}_2\text{SO}_4$ ; barium sulphide +  $\text{FeSO}_4$ , etc. etc.

\* Creosote oil is a coal-tar fraction, of sp. gr. 1.09 at 20° C., distilling between 210°-355° C. It should contain little free carbon.

† Formerly mercuric chloride, zinc chloride and copper sulphate were the only water-soluble preservatives, but they have now been largely superseded by the mixtures of chemicals shown on p. 191.



*Gautsche* (German Patent, 152,006) renders wood "fireproof" by removing air *in vacuo*, and then impregnating under pressure with ammonium sulphate and borate at 50° C. Such wood will only *char* to a depth of 1 cm., and will not spread fire.

*Hasselmann* impregnates wood under pressure with boiling solutions of iron and copper salts. Wood is also made fireproof (superficially) by painting with sodium silicate.

(c) **Surface-Charring Wood.**—This is an old process, and consists in scorching the surface of the wood with blowpipe flames, and rubbing off the charcoal produced, thus giving a smooth, hard, brown surface, very resistant to moisture and rot. It does not protect the *interior* parts of wood from dry rot should these be infected before carbonisation. The heating of the wood on the surface causes it to be impregnated with tarry matters, and this explains the preserving effect.

(d) **Drying Wood.**—Wood is always "seasoned" or air-dried for a considerable time—sometimes two to three years—before being used, by the simple process of stacking under a shed so that air has full access around and between the planks. Imperfectly dried timber will not only easily warp, but is very susceptible to dry rot, mildew, etc. Sometimes, after stacking, the wood is dried in a stream of hot air at 30°-150° C., the wood being placed in large heated chambers for the purpose, and the heating being carried out very gradually, otherwise the wood will split or warp. The dried wood is usually brushed over with tar, linseed oil, paint, etc. "Green timber" contains 40-60 per cent. water, but "air-dry" timber 10-12 per cent. When the moisture content falls below 10 per cent. wood-destroying fungus cannot develop.

(e) The **sap** of the tree, containing albuminous matter, sugars, etc., easily becomes decomposed and sets up putrefaction, and nourishes insects, etc. The tendency is lessened by withdrawing the sap, (a) by soaking in water, (b) better by steaming in enclosed iron apparatus with steam pressure, or simply (but less satisfactory) by sixty to seventy-two hours' steaming in wooden vessels.

**Making Wood Non-Inflammable.**—The following means are in use:—  
(1) Painting with water-glass solution; this is probably the best material;  
(2) impregnating with alum followed by lime, or impregnating with sodium or potassium carbonate, followed by an alum solution; (3) other impregnating solutions, especially for fire-protection, are copper sulphate, zinc chloride, ammonium sulphate and gypsum, borax and magnesium sulphate. See under **Metallisation** above. For methods of making fabrics non-inflammable see Section XVII., Part III., Textile Fibre Industry, p. 527.

#### Addendum of Timber—Preserving Chemicals (1948)

The principal water-soluble preservatives now on the market may be classified into the following groups:—

1. Mixtures of chromates, dinitrophenates and fluorides.
2. Copper salts with or without the addition of arsenates and chromates as fixatives.
3. Chromated zinc chloride.
4. Organic dyestuffs, *e.g.*, nitrochlorhydroxy toluenes.
5. Borax solutions (5 per cent.).

Toxic chemicals dissolved in volatile oils have come to the fore in the last decade. These are usually copper and zinc naphthenates,  $\beta$ -naphthol and pentachlorophenol.

A very lucid treatment of the whole subject of wood preservation is given in the above-mentioned "Decay of Timber and its Prevention."



### III.—WOOD PULP FOR PAPER

#### LITERATURE

CROSS AND BEVAN.—“Wood Pulp.” London, 1911.

MAX SCHUBERT.—“Die Holzstoff oder Holzschiff-Fabrikation.” 2nd Ed. Berlin, 1909.

„ “Die Cellulosefabrikation.” Berlin, 1906.

C. PIEST.—“Die Zellulose.” Stuttgart, 1910.

See also the general works mentioned under Cellulose, p. 187.

#### Mechanical Wood Pulp for Paper

The wood blocks, after a preliminary steaming, are pressed against a revolving grindstone, which reduces the material to a fine condition, but not to a powdery form. The disintegrated fibre is pressed against a wire screen, which allows the finer particles to pass through, retaining the coarser particles for further treatment. **Voelter's wood-pulping apparatus** is shown in Fig. 70.

A is the pulping apparatus, with the vat K in which the revolving grindstone S is placed. The blocks of wood are forced against the circumference of the revolving stone by the arms *pp*. Water is introduced at G, and the revolving stone carries the pulp against the screen E, which admits the passage of the finer particles of the wood, while the coarser particles pass away through an oscillating basket placed in the trough into the refining cylinder B, which retains the coarser particles; thence it passes through the distributing apparatus and hopper C to the refining cylinder D. The refining cylinders are covered with fine gauze wire sieves. The ground material which fails to pass through the sieves, is ground up by millstones E, the united pulp being mixed in the tank F, and passed successively from the circumference into the sieving cylinders G, H, and I, thereby removing all coarse particles from the pulp; the rejected coarse particles are ground down by grinding stones and sieved again.

Mechanical wood pulp is only used for making inferior grades of paper, such as news and wrapping, because such paper is difficult to bleach white, and on exposure to sunlight, or on keeping, turns yellow.

The presence of mechanical wood in paper can be easily detected, since such paper gives a purple stain when moistened with a mixture of phloroglucin and hydrochloric acid, while a solution of aniline hydrochloride colours it deep yellow.

The colouring is due to the encrusting matter, the lignin, which surrounds the cellulose fibres of the wood, and forms about 30 per cent. of the wood, the rest being cellulose (60–70 per cent.), resin, and similar products.

**Statistics.**—The United Kingdom in 1910 imported 8,500 tons of **dry** and 480,700 tons of **wet** mechanical wood pulp, of total value £1,160,000. 311,000 tons were obtained from Scandinavia. The United States in 1909 imported 109,000 tons of mechanical wood, value, \$2,058,000.

For modern statistics see Appendix III.

#### Chemical Wood Pulp (Pure Cellulose)

As mentioned above, ordinary wood fibres do not consist of pure cellulose, but are encrusted with **lignin**, **xylan**, and other complex substances, which cement the cells together into a stiff mass. Ordinary wood contains only about 60–70 per cent. of cellulose, the rest consisting of encrusting substances, resins, etc., all of which must be removed by chemicals before such cellulose can be used for making the better qualities of paper, as the paper otherwise turns yellow and is weak. The encrustations are removed by several methods.

**The Sulphite Process.**—This is principally used in Scandinavia and Germany, about 560,000 tons of cellulose being yearly manufactured by the



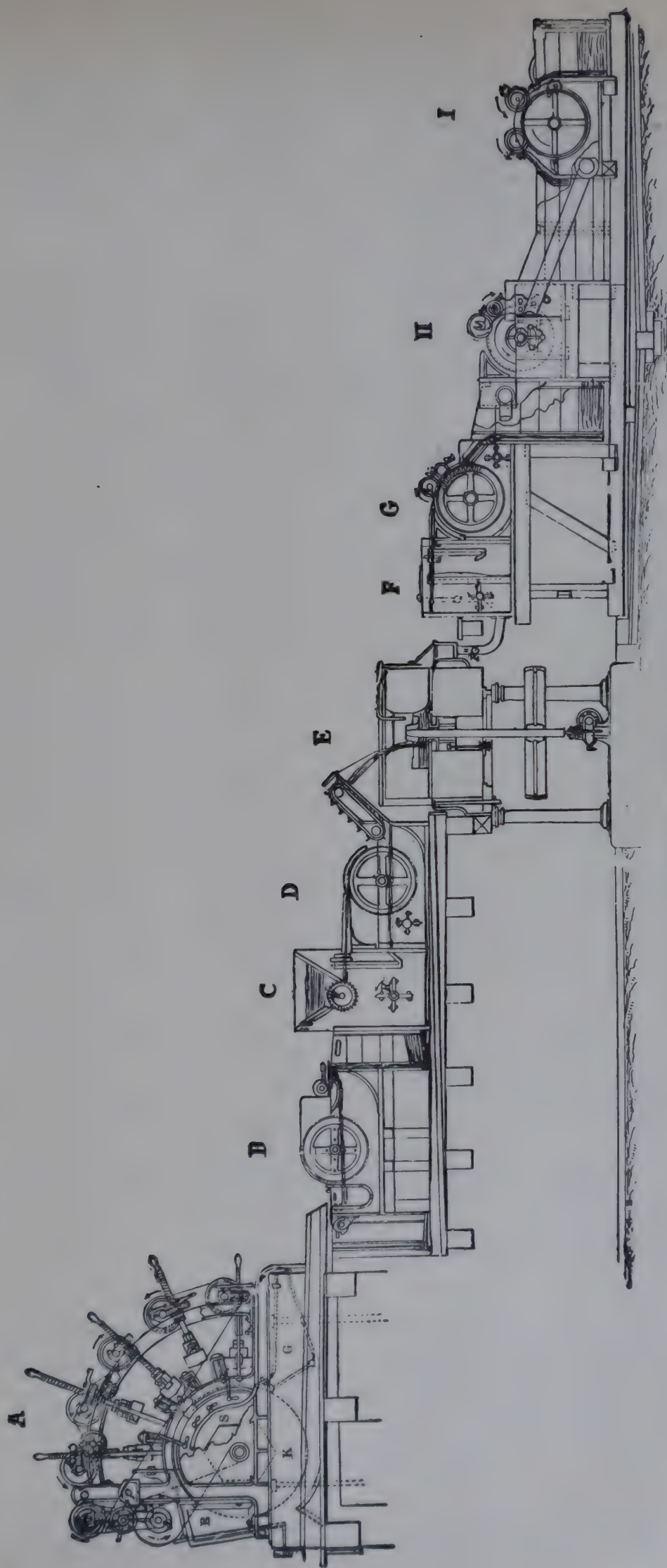


FIG. 70.—Voelter's Wood Pulp Machine.

process (*Z. angew. Ch.*, 1907, 610). It was patented in 1866 by Tilghman, and worked on the large scale by Ekman and Mitscherlich.

The wood—usually pine—has the bark removed, and is then cut by rotating knives into thin slices about 1 mm. thick. The wood is then (usually) steamed, and the brown waste water run away; next it is introduced into large boilers (12 yds. long  $\times$  4 yds. diameter) and heated for several hours with a solution of calcium bisulphite, which is produced as follows (Mitscherlich):—

Iron pyrites,  $\text{FeS}_2$ , is roasted in furnaces similar to those used in the manufacture of sulphuric acid. The gases, rich in sulphur dioxide, which pass away up the flues, are led in at the base of a tall tower, which is from 30-90 ft. high and about 6 ft. in diameter: the tower is filled with chalk or limestones, which rest on a series of gratings placed at intervals up the tower. A stream of water trickles over the limestones, entering at the top of the tower and escaping at the base.

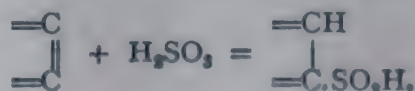
The sulphur dioxide in the ascending gas is absorbed by the water to form a solution of sulphurous acid; the acid solution then attacks the limestone, forming a solution of calcium bisulphite. Often the gases are allowed to pass through several such towers in succession, until a sulphite solution of requisite strength is obtained. The solution used for boiling should have a density of  $4^\circ\text{--}5^\circ$  Bé., and contain 30 g. sulphurous acid (as determined by iodine solution) per litre, 25-33 per cent. of the sulphurous acid being united to calcium in the form of calcium sulphite. The solution also contains some calcium sulphate, owing to the oxidation of sulphurous acid. Each cubic foot of wood requires about  $1\frac{1}{2}$  cub. ft. of sulphite solution.

Since the sulphurous acid rapidly attacks the iron of the boiler, the latter must be protected on the inside against the corrosive solution. This was formerly achieved by an internal coating of lead. This, however, has now been abandoned in favour of a layer of acid-resisting tiles embedded in cement, the joints being luted with a mixture of lead oxide and glycerol (100  $\text{PbO}$  : 12 glycerol), or with a mixture of Chamotte powder, cement, and water glass. If the iron is not protected the corrosion is such that explosions of the boiler may occur.

The boiler is heated by indirect steam (steam coils) to a temperature of  $115^\circ\text{--}120^\circ$  C., under a pressure of  $2\frac{1}{2}$ -4 atmospheres. The wood is heated for twenty-four to forty-eight hours. *Ritter-Kellner* heats to  $140^\circ\text{--}150^\circ$  C. with free steam for eight to sixteen hours under 4-6 atmospheres. This process is much quicker, but yields a softer and weaker cellulose than that obtained by Mitscherlich's process.

Occasionally small rotating boilers are used in order to ensure thorough mixing; sometimes two or more boilers are united together to form a system, with the object of utilising the lye twice. When the process of boiling is finished—which is determined by withdrawing a sample of the sulphite liquor and estimating the  $\text{SO}_2$  in it, the percentage of which greatly diminishes owing to its absorption by the wood—the boiler is blown, the escaping  $\text{SO}_2$  being led into the sulphite towers. Next the brown solution is run off, and the cellulose washed once with water in the boiler. The wood by this treatment has been resolved into a mass of cellulose fibres, which can be pressed easily into a paste. All the encrusting substances have been dissolved and passed away with the sulphite solution.

The exact nature of the changes which take place are not thoroughly understood, being, doubtless, of a very complex nature. According to *Klein* (*Papierzeitung*, 1906, 167), the calcium salt of ligninsulphonic acid,  $\text{C}_{18}\text{H}_{19}\text{O}_8\text{SCa}$ , is produced. According to *Klason*, lignin has a constitution similar to a glucoside, being formed by the combination of aromatic substances and sugars or cellulose: it contains the oxypropylene group,  $\text{CH}=\text{CH}.\text{CH}_2\text{OH}$ , as well as aldehyde, methoxy and hydroxy groups. During the process of boiling the sulphite unites thus:—



In the compound thus produced the  $\text{SO}_2$  is so firmly fixed that it does not exert reducing properties, and does not affect iodine, nor is it liberated by  $\text{H}_2\text{SO}_4$ . The sulphite solution also



contains various sugars, such as dextrose from cellulose, xylose,  $C_5H_{10}O_5$ , from xylan, tannic acid, resins, proteids, acetic acid, etc.

The cellulose fibres in the boiler must now be carefully freed from twigs, unacted-on wood, knots, dirt, etc., which otherwise would form black specks in the paper. For this purpose it is crushed in special machines, and pulped in Hollanders, the pulp being finally purified from dirt, splinters, etc., by a careful sieving process, the residues being ground up and worked again. Finally the refined wood cellulose is poured on to a wire cloth, as in paper-making, and obtained in the form of thick sheets; it is dried on hot rollers and sent to the paper mills as "**Half-stuff**." The substance is almost white, but for making the best sorts of white paper it is bleached with chloride of lime and acid, or by electrolytic processes, as is described under **Paper**. This treatment destroys any residual lignin which may still remain in the cellulose pulp. 100 parts by weight of wood yield 40-45 parts by weight of cellulose, the rest going into solution.

**Treatment of the Waste Sulphite Lye.**—We have just mentioned that over 50 per cent. of the weight of the wood goes into solution in the sulphite lye in the form of the calcium salt of lignin-sulphonic acid,  $(C_{18}H_{19}O_8SCa)$ , the acid being a gummy body. The lye also contains important quantities of dextrose (from the cellulose), xylose,  $C_5H_{10}O_5$ , resins, acetic acid, tannins, and gummy matters. It is usually neutralised and filtered from fibres and allowed to run to waste into the rivers, thereby greatly polluting them. Great efforts have been made to find an industrial use for these liquors, the adequate, harmless disposal being an important industrial problem of the present day, and one which is causing increasing anxiety to the large cellulose factories.

In Sweden, the lye is neutralised, and the sugars fermented and worked for industrial alcohol (p. 294).

In several factories the lye is concentrated, when a gummy liquor is obtained which is used as a sizing and finishing agent. The residues forming the black "**Cellulose Pitch**" have been used for briquettes. By special methods extracts are obtained which are useful in leather manufacture. (See German Patents, Nos. 75,351, 183,415, 194,872, 86,651, 93,944, 93,945, 122,489). The lignosulphite in solution has been used in medicine as a cure for consumption.

**The Soda Process.**—This process is principally carried on in America, where over 75 per cent. of the cellulose is manufactured by this process. On account of its high cost compared with the sulphite process, and of the evil-smelling gases evolved, the process is only employed to a very limited extent in Europe, principally for **straw**, as the silica encrustations cause difficulties in working it by the sulphite method. The wood, dried and cut up as in the sulphite process, is placed in gas-heated boilers and heated with caustic soda solution of  $12^\circ B\acute{e}$ . under a pressure of 6-10 atmospheres. The caustic soda dissolves the lignin, resin, etc. etc., and to some extent attacks the cellulose itself, so that the action is more deep-seated, and the yield less, than in the case of the sulphite process. The soda solution becomes almost black. If straw is to be treated, it is cut up, and heated to 3-5 atmospheres, with a somewhat weaker soda solution than is used for wood.

In either case the cellulose must be carefully washed, resolved into fibres, and bleached before it can be incorporated into fine paper.

The soda lye must be regenerated. It is evaporated *in vacuo* and then calcined, whereby the organic matter is destroyed. The sodium carbonate is extracted by lixiviation with water and is causticised by lime.

In each operation about 10-12 per cent. of soda is lost. The loss is made good by sodium sulphate or carbonate.

The "**sulphate**" process is a modification of the soda process, sodium sulphate being the exclusive source of the alkali; this is reduced to  $Na_2S$  in evaporating and igniting the lye from the boiled wood. The evil-smelling gases evolved (mercaptans, etc.) are a great objection to the process.

Recently an increased demand has been made for a white "**half-stuff**" intermediate between mechanical wood pulp and cellulose; the Swedes meet this want by boiling the wood with an insufficient amount of soda for complete action. The product is used in making strong packing papers with a good "**rattle**," and is known as "**Kraft**" papers.

Cellulose may be manufactured from the refuse fibres of the cotton seed which remain on the seed shells after the cotton has passed through the ginning mill and which are waste products in the process of cotton manufacture. Fats, oils, and



resins are first extracted with naphtha, and the fibres are then boiled with caustic alkaline lye. (See German Patent, 134,263.)

**Kellner's Electrolytic Process for preparing Cellulose** depends upon the formation of caustic soda, free chlorine, and hypochlorous acid when an electric current of suitable strength is passed through brine.

The boilers A and B, Fig. 71, are charged with wood through manholes D, and then brine is run in until the level rises to the boiler C, as is shown by the water glass E. The temperature is brought to 262.4° F. (117° C.) by steam coils when the current is passed. The gases rise through the apparatus and pass into a condenser G. Every fifteen minutes or so the current is reversed so that alternately the pulp in either boiler is subjected to the action of NaOH and then to the action of Cl and HClO. This process is becoming increasingly popular. (See the French Patent, 326,313, and the American Patent, 773,941.)

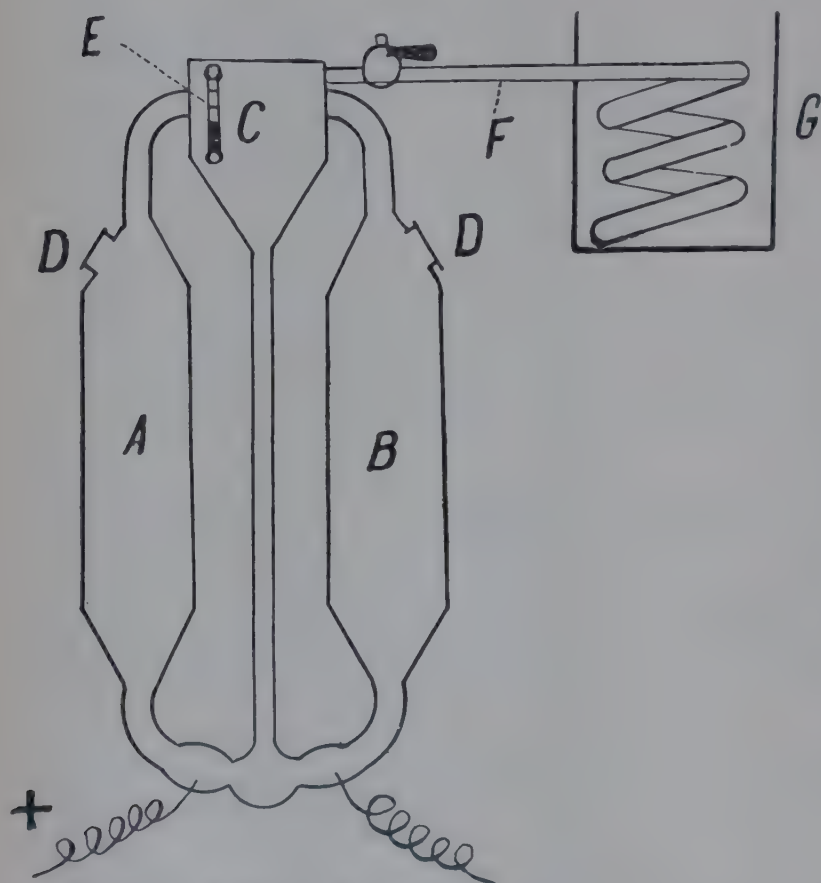


FIG. 71.—Kellner's Electrolytic Process for preparing Cellulose from Wood.

According to **Bühler's Process** (German Patent, 94,467) cellulose is also prepared from wood by treating it with tar oils containing phenols at a temperature over 150° C.

#### **Bleaching Pulp obtained by the above described Alkaline or Sulphate Processes.—**

Bleaching powder is usually employed, although Na and magnesium hypochlorites are sometimes used, and also, as in the Hermite process, an oxidising solution obtained by electrolysing a solution of  $MgCl_2$  or other chloride.

**Pure Cellulose** may be obtained by boiling cotton, flax, hemp, etc., with a solution of NaOH of about 1-2 per cent. strength, washing, exposing to the action of chlorine gas or bromine water at the ordinary temperature, and again boiling with sodium hydrate, sulphate, or carbonate. Fats and resinous products,

produced as by-products during the halogen treatment, are extracted by means of alcohol and ether. The best filter papers are practically pure cellulose. They are treated with hydrofluoric acid to remove mineral matter and leave a minimum of ash.

**The Wood Cellulose** obtained by the various processes above described consists of a soft mass of fine fibres (Fig. 73), each fibre being made up of an elongated cell somewhat resembling that of a cotton fibre, but much shorter (3-5 mm. long against 20-70 mm. for cotton).

Fig. 72 shows wood cellulose fibres—1 and 2 representing cells magnified to different degrees, while 3 represents a section. It will be seen that the fibres are hollow, with pointed ends, and provided with a number of minute pores *a, a, a* running right through the cell walls. See 4, Fig. 72, for a section through a pore.

**Statistics.**—In 1910 England imported 350,000 tons of **dry** and 20,000 tons of **wet** chemical wood pulp, of total value £2,340,000. Of this, no less than 299,000 tons came from Scandinavia.

The United States imported in 1909, 157,000 tons (value \$6,600,000), and in 1910, 234,000



tons (value \$9,200,000). The export was 9,200 tons (value \$449,000) in 1909, and 7,900 tons (value \$360,000) in 1910.

For modern statistics see Appendix III.

**Wood-Cellulose Cloth and Yarn.**—Attempts have frequently been made to spin the cellulose pulp into cloth, but the fibres have always proved too short. The firm *Altdamm* near Stettin, however, appears to have solved the problem by forcing the pulp through narrow gutters, and then converting the narrow flat ribbons thus produced by a rolling motion into spinnable fibres. Ropes, cloth, and even clothes have been thus made from paper pulp. The dry cloth is fairly strong, but the wet is very weak.

The yarns are placed on the market under the names silvalin, xylolin, licella fabrics, etc., and form a cheap substitute for cotton and flaxen yarns. (See German Patents, 136,371, 142,678, 149,444, 159,418, 167,490.)

**Hydrocellulose**,  $C_{12}H_{22}O_{11}$ , is manufactured on the large scale because it yields a gun-cotton more readily exploded by concussion than ordinary gun-cotton. The process is as follows: Pure cotton is immersed for three or four minutes in a solution of 3 parts of concentrated  $H_2SO_4$  or  $HCl$  in 97 parts of water. The cotton is freed from adhering liquor, dried, heated at a temperature of  $104^{\circ}$ - $158^{\circ}$  F. in stoneware vessels for three to ten hours, washed, and again dried.

Another process (German Patent, 123,122) treats cellulose with a small amount of  $KClO_3$  and  $HCl$ , keeping the temperature at  $60^{\circ}$ - $70^{\circ}$  C. It forms a white powder, not very sensitive to acids or alkalis, and so is used for making acid proof or alkali-proof articles. When the mixture is treated with  $S_2Cl_2$ , and the product poured into water, a sulphur-hydrocellulose is produced (German Patent, 137,206), which can be used for vulcanising rubber, both the cellulose and sulphur combining with the rubber.



FIG. 73.—Wood Cellulose Fibres.

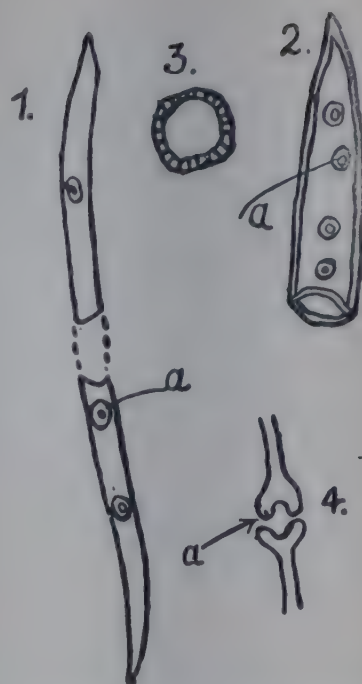


FIG. 72.—Cellulose Cells (Wood Fibres)—(1) Fibre; (2) the same enlarged; (3) section of 2; (4) section of wall or cell through a pore; a, a, a, pores.

**Oxycellulose**,  $C_6H_{10}O_6$  or  $C_6H_8O_6$ , is obtained by the action of mild oxidising agents on cellulose, e.g., by treating cotton with  $NaOH$  + dil.  $KMnO_4$  solution ( $\frac{N}{10}$  solution), or by boiling filter paper with two and a half times its weight of dil.  $HNO_3$  (sp. gr., 1.3). Several kinds of oxycelluloses are known. They are used for obtaining a damask effect in the cotton industry.

Hydrocellulose and oxycellulose both readily reduce Fehling's solution, and are thus distinguished from normal cellulose.

## IV.—PAPER-MAKING

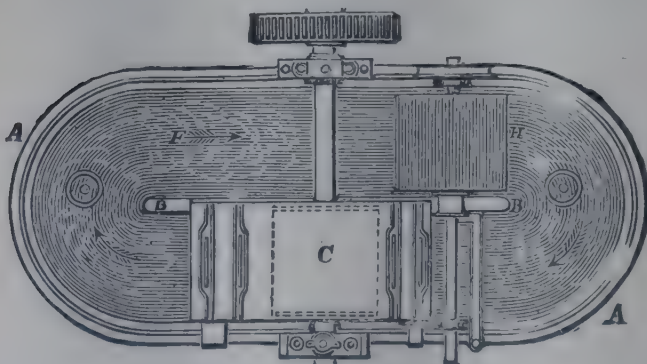
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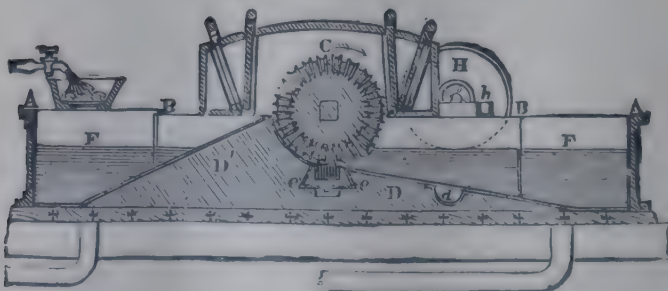
**The Materials** used consist of linen rags, esparto grass, wood-pulp, mechanically powdered wood, etc. etc. The bulk of paper produced is made from wood and esparto. After the materials have been well boiled with soda or other cleansing chemical to free them from dirt and extraneous matter, the crude product is next transferred to a cutting or pulping engine called a “Hollander.” It consists of a cast-iron trough A, Fig. 74, about 10 ft. long,  $4\frac{1}{2}$  ft. wide, and  $2\frac{1}{2}$  ft. deep, rounded at the ends. It is provided with a partition called the *midfeather* BB, of such a length as to have the trough of uniform width round it. A cylinder

or *roll* C, furnished with a series of steel knives, rotates in one of the divisions formed by the midfeather; the floor of the trough in this division is inclined in such a manner as to cause the pulp as it travels to pass under the roll. If the machine is to be used for cutting rags or similar material (not grass) a *bedplate* is placed beneath the roll; this is fitted with a series of steel knives similar to those on the exterior of the roll. The distance between the knives of the roll and the bedplate is regulated by levelling screws, so that the material may be cut to any required degree of fineness. The drum washer H is covered with fine-wire gauze or cloth, and allows water to run away (or enter) without any of the pulp fibres passing out with it.

The object of the knives is not so much to shorten the fibres by cutting—as this would weaken the resulting paper—but to draw them



Hollander, Ground Plan.



Hollander, Sectional View.

(See also Fig. 244, p. 628.)

FIG. 74.

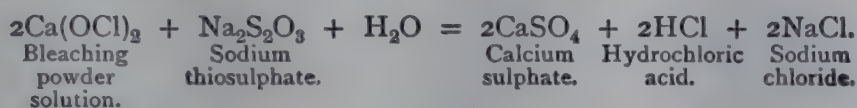


apart and separate them. The material is worked in the hollander until cut up into the necessary fine state of division, when it is known as "**Half-stuff.**"

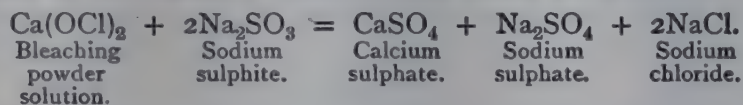
The half-stuff is run from the hollander into a mixing engine called the "potcher" or "poacher," where it is agitated with the necessary quantity of bleaching liquor, chloride of lime and dil. HCl or H<sub>2</sub>SO<sub>4</sub> being usually employed, although in recent years processes of electrolytic bleaching are coming into use.

From the bleaching apparatus the half-stuff is now run into a "beating engine." This is similar to the hollander previously described, but the knives of this engine are more numerous, and revolve more rapidly. This machine achieves the purpose of washing the half-stuff free from bleaching material and acid, and reducing the half-stuff to a slightly finer state of division necessary to make the fibres "felt" (*i.e.*, intertwine) well together on the shaking wire of the paper machine. It also serves as a mixing engine for loading, sizing, and colouring the paper pulp before actually making it into paper.

Before sizing, the last traces of chlorine are removed by treating the pulp with "antichlor." For this purpose sodium thiosulphate is usually employed, which decomposes any bleaching powder still in the fibre, thus:—



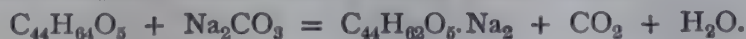
Sodium sulphite is now largely used for the same purpose:—



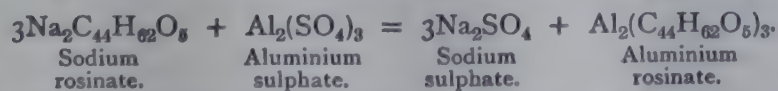
Although three times as much of sodium sulphite is required to produce the same effect as a given amount of sodium thiosulphate, yet the sulphite is preferred by paper-makers, as no free acid is formed, which would corrode the wire of the paper-making machine. Hydrogen peroxide also produces excellent results, but is too costly. The presence of bleaching powder in the stuff is determined by testing with KI+starch solution. The chlorine sets free iodine, which colours the starch blue. Hence the addition of antichlor to the pulp is continued until the latter ceases to give a blue stain with KI+starch solution.

**Sizing.**—Unsize pulp, as it comes from the bleaching tank, is bibulous, and if made into a paper with the addition of a little starch as binding material, forms what is known as "blotting paper." Such paper is very weak. Writing or printing paper must be "sized" so that they acquire a water and ink resisting quality.

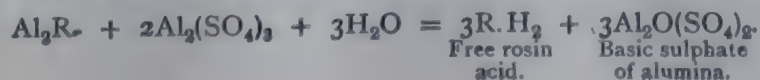
**Engine sizing** (Rosin-alum-sizing) is used for writing and wrapping papers. When rosin—which is abietic acid, C<sub>44</sub>H<sub>64</sub>O<sub>5</sub>, or its anhydride—is heated with a solution of alkalies it rapidly dissolves, forming rosin soaps.



100 parts of rosin require 15-18 parts of sodium carbonate to form a "neutral" rosinate. Sometimes starch solution is added. The rosin soap is now added to the paper, 100 lbs. paper requiring 3-4 lbs. of the original rosin. Then after thorough mixing a solution of **alum** or aluminium sulphate is added, and this decomposes the sodium rosinate, the insoluble aluminium rosinate being precipitated thus:—



100 parts rosin should, theoretically, require 23 lbs. of alum—as a matter of fact, over three times as much is used. The aluminium rosinate precipitated in the paper pulp was supposed to be the sizing agent, which makes the paper non-absorbing of ink. C. Wurster concludes that the *effective* sizing agents are *free* rosin acids (since paper extracted with ether loses its water-resisting properties with the removal of the free rosin acids), and the function of the *excess* of alum is to decompose the neutral rosinate of alumina with liberation of the free acid, thus:—





R stands for  $C_{44}H_{62}O_5$ , the radicle of abietic acid,  $C_{44}H_{62}O_5H_2$ .

Among auxiliary agents used in sizing may be mentioned **starch**, alumina, soap, and cellulose hydrates. The latter constitutes viscose sizing (see under **Viscose**), the viscose being added to the pulp, mixed, and decomposed by adding zinc or magnesium sulphate. The fibres thus become coated with a film of

**gelatinous** cellulose, which exerts a powerful cementing action in making and drying. Such paper is very strong, but the process does not seem to have been adopted to any large extent.

**Silicate of Soda and Casein**—the albuminoid substances contained in milk—are also sometimes used in sizing. Casein is coming more into use, being added to the pulp in the form of a strong solution, which is completely precipitated by alum; it imparts toughness and a good "handle" to the finished paper. Sometimes the casein is mixed with sodium silicate.

If the sizing takes place after the conversion of the material into paper (surface sizing), animal size alone is used.

**Mineral Filling and Loading Agents.**—It is usual to add to the pulp a quantity of a cheap mineral loading material to make the paper more suitable for the particular purpose to which it is applied. **Kaolin** or **china clay** is the loading usually employed in making **news**, **printing**, and low-grade writing paper. The clay is added to the pulp after making into a cream with water. The addition of clay serves to fill up the pores of the paper, giving

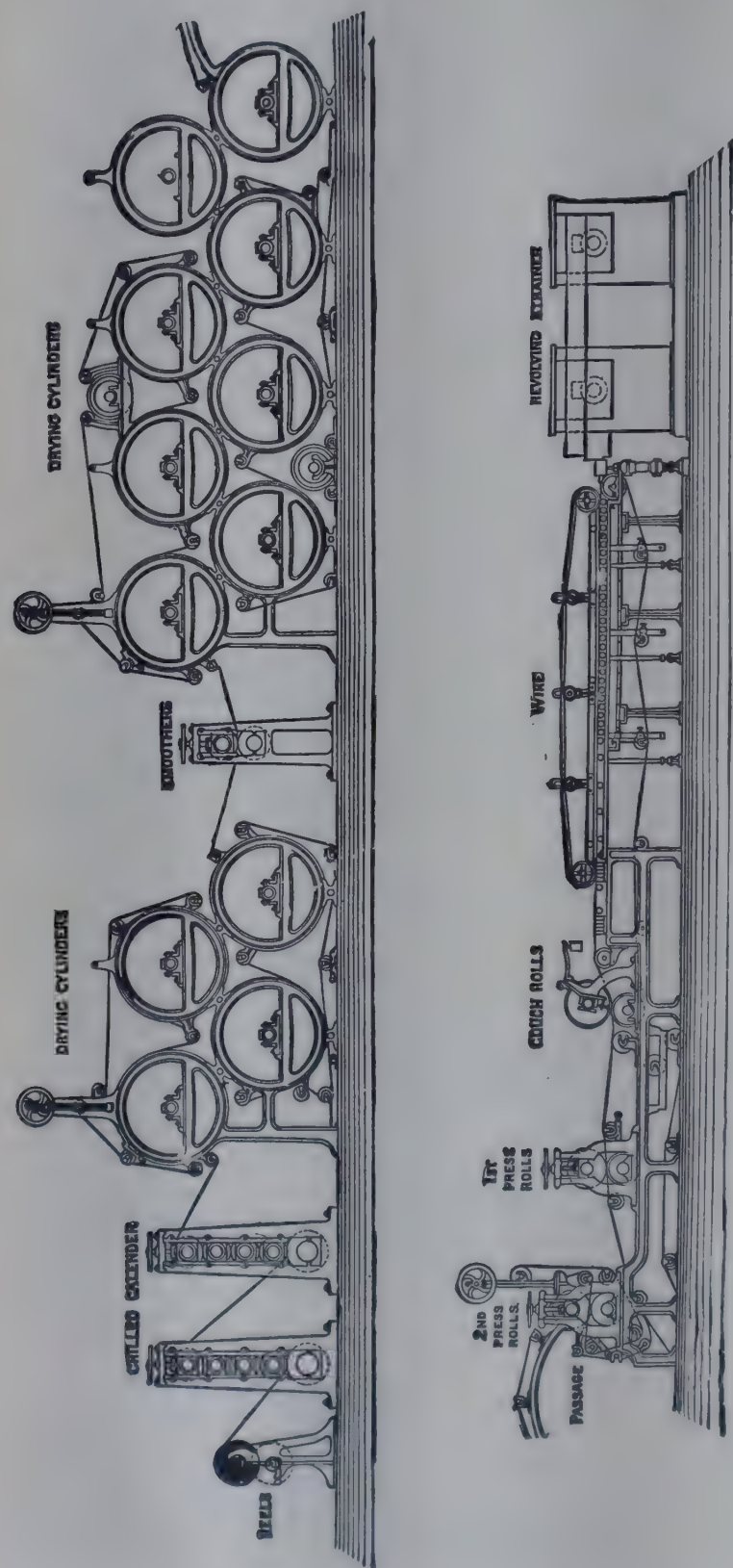


FIG. 75.—Fourdrinier Paper Machine.

a smoother surface and increasing its absorbent power for printing ink, and also gives an improved surface in calendering. It also adds to the opacity of the paper.

For the better qualities of writing papers the materials used are calcium sulphate ("pearl hardening"), barium sulphate, barium chloride, and **agulite**, a fibrous-like mineral like asbestos.



**Starch** is always applied to papers in the process of manufacture, for the same reason that it is used in laundries for preparing collars and cuffs, viz., to give it a fine polish and hardening effect in the subsequent glazing process, when the paper is passed through hot iron rolls.

**Colouring.**—The bleached pulp has always a yellowish tint. This is removed by mixing in **blue** ultramarine, smalt, or similar “correcting” colour, a pure white-looking paper then resulting.

The colouring of paper is either effected by grinding suitable pigments into the pulp or using suitable aniline colours for dyeing the pulp.

**Paper Machines.**—The pulp is now ready for making into paper. The pulp, properly sized, loaded, and coloured, is discharged from the mixing engine, through strainers, into the paper-making machine, usually known as the **Fourdrinier**. (See Fig. 75.)

It consists of an endless wire-cloth from 32-50 ft. in length and almost any width up to 126 in., travelling at the rate of 100-300 ft. per minute. The wire-cloth is made of exceedingly fine wire, the meshes ranging from sixty threads upwards to the inch. The pulp, after it leaves the beating engine for conversion into paper, passes first into large cylindrical vessels known as “stuff-chests,” containing rotating arms to keep the pulp and water intimately mixed. Thence it runs into straining machines, and thence into a vat provided with a horizontal agitator; from the vat it flows on to the endless wire-cloth of the paper-machine. The wire-cloth is

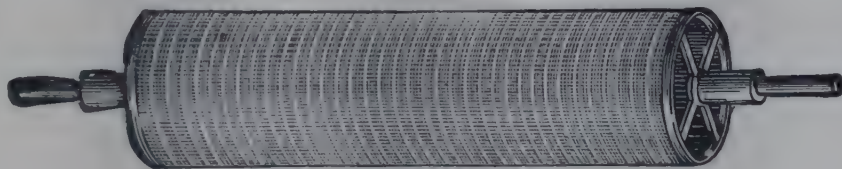


FIG. 76.—Dandy-Roll.

supported by a series of brass tube rolls, carried upon brass bearings, and motion is given to it by the rotating couch-roll at the end. When it is required to produce a design or name, called a *water-mark*, upon the paper, this is done by means of a roll called the *dandy-roll*, which consists of a skeleton roll covered with wire-cloth, upon which the design is worked by means of very fine wire. At the extreme end of the wire-cloth, and inside the wire, is the *under couch-roll*, from which the wire receives its motion. Above this is the *upper couch-roll*; both rolls are covered with felt, the upper roll resting upon the lower one. The wire-cloth with the web of paper upon it passes between the rolls, receiving gentle pressure, by means of which the paper becomes deprived of much water, rendering the paper compact. Here the web of paper leaves the wire-cloth, and passes on to a continuously revolving and endless web of woollen felt, called the “wet felt,” about 20 ft. long and carried on wooden rollers. The paper then passes to the *first press-rolls*, which deprives it of a further quantity of water; the surface of the paper is then reversed in the *second press-rolls*, so that both sides of the paper are brought into the same condition. From the press-rolls the paper passes to the drying cylinders, which are heated by steam. The paper slowly passing over their surface is dried and brought into a proper condition for passing between the *smoothing-rolls*, also heated by steam, which give the paper a fine smooth surface. The paper then passes over another series of drying cylinders, where it is perfectly dried. The paper now passes through the *calender rolls*, hot polished rolls, where it receives a fine glaze; finally it is wound on to the reels at the extreme end of the machinery. The paper is then cut by special machinery into sheets of any required dimensions.

The strength of paper is largely determined by the length of the fibres—the longer the fibres the stronger the paper.



Wood cellulose is now one of the most important materials for paper-making. Cheap printing papers contain 50-80 per cent. of mechanical wood pulp. The better qualities of writing paper consist of pulped linen rags. The best and most permanent sorts of paper—such as employed for legal documents—are made of pure linen or hemp fibres.

**Parchment Paper**, which is extensively used for covering jars and pots for pickles and jams, and for binding books, is made by dipping white unsized paper for a few seconds into concentrated sulphuric acid and washing free from acid with dilute ammonia. The cellulose has been turned by this treatment into a hydro-cellulose, and is impervious to grease, water, etc. Coloured parchment paper is used as a leather substitute.

The conversion of cellulose into gelatinous hydrocellulose can also be effected by the wet-milling processes employed by the paper-maker. Thus a "*grease-proof imitation parchment paper*" is obtained by pressing, crushing, and rubbing the fibres for a long time in the presence of water, *wood sulphite-cellulose* being usually ground up in a special Hollander provided with blunt knives. Ultimately the cellulose absorbs water and a slimy mass is obtained, which makes the translucent paper so largely used as a packing for butter, sausages, and other provisions, since it is impervious to fat. This paper has no loading or sizing material, with the exception of a little starch, and is strongly calendered. If such paper is warmed over the point of a small candle flame tiny bubbles appear—due to steam which cannot escape through the water-tight surface of the paper. This is used as a test for its fat-proof quality.

"**Cellulith**" is obtained by carrying the mechanical hydration to its fullest extent. The cellulose is ground with water for 40-150 hours, when the fibrous structure is completely broken down, with the production of an amorphous cellulose jelly. This is boiled for two hours to expel air, and then hardens on drying to a product of the consistence of bone. This mass can be mechanically worked and polished like horn, bone, or ebonite, and is used as a binding-agent for carborundum or emery wheels, and as a packing-material for making tight the covers of autoclaves, etc. It withstands the action of alcohol, ether, petroleum, fats, and oils.

**Waterproof Papers** are usually made by passing paper through a cellulose solvent, such as copper hydroxide dissolved in ammonia (cuprammonium). The fibres are cemented together by the solvent action of the cuprammonium, and when dried acquire a varnish-like surface. A strong solution of zinc chloride acts in a similar way. Sheets of paper treated with concentrated zinc chloride solution are placed one on the other and pressed or rolled by hot rolls into thick homogeneous solid plates resembling thick sole-leather. Paper treated in this way is known as "*vulcanised fibre*" and is made pliable by soaking in glycerin. It is used as a water-tight isolating and packing material, for pumps, etc. etc. Such blocks may be bored, turned, polished, and coloured. (See Marshall, *Ch. Z.*, 1908, Rep. S. 544. Also Piest, "*Die Zellulose*," Stuttgart, 1910.) \*

**Papier-Maché** is made of paper pulp and binding materials, the mass being moulded. Some sorts are made by cementing together sheets of paper. A flexible, impenetrable, and acid-proof composition is obtained by moulding a pulp made of 15 per cent. rags and 85 per cent. cellulose, drying by hot air, steeping in solutions of resin oils, drying, and again steeping.

**Cardboard** may be made like paper, by pouring the pulp on to wire frames until it is thick enough. The product is weak. The better sorts are made by pressing moist, quite freshly-made sheets of paper one on the other. They adhere under pressure, and form a solid mass called "*couché pasteboard*." Carton pasteboard is made by pasting finished and dried leaves of paper one over another till the proper thickness is attained. Sometimes tar and crushed stones, asphalt, etc.

\* See under "The Plastics Industry" for the treatment of paper with plastics for waterproofing.



are mixed into the paper pulp for making roofing or tar pasteboard. **Carton Pierre** for roofing is made this way.

**Testing Paper.**—The mechanical tests for paper (strength, etc.) are usually carried out with special apparatus, which are described in Allen's "Commercial Organic Analysis," vol. i. p. 467.

**The Ash** is determined by drying 1-2 g. to constancy at 100°-105° C., and igniting in a platinum (or porcelain) crucible until the weight is constant. If the paper contains lead compounds, this will attack the platinum, and the determination must be carried out in a porcelain crucible. A qualitative analysis of the ash reveals the mineral loading-agents used.

The **presence of Mechanical Wood** is shown by moistening with (1) a solution of phloroglucinol acidified with HCl, which gives a purple colour with wood; or (2) aniline sulphate solution, which gives a yellow colour with wood.

The **Sizing** is tested by *Leonhardt's* method: the paper is moistened with one drop of a 1.5 per cent. ferric chloride solution for as many seconds as the weight of the paper in grams per square metre. Then the paper is dried with blotting-paper, and the back is painted with a 1 per cent. tannin solution. With well-sized papers no coloration should take place, badly sized papers colour almost immediately, moderately sized in about sixty seconds. Rosin in the size is detected by boiling with absolute alcohol + a little acetic acid, and a milkiness is produced on pouring into water, or by extracting paper with ether and evaporating, when a layer of rosin is left.

**Animal Size** (glue, gelatine) is detected by boiling the paper (10 g.) with a little water, filtering, evaporating to small bulk, and adding tannin solution. A greyish precipitate, *not turned blue* by I+KI solution, shows animal size. Starch also gives a precipitate with tannin, but this is turned blue by the iodine solution.

The **fibrous** constituents of paper are usually determined by a microscopic examination; the application of certain staining chemicals also helps to differentiate between them. The following table shows this:—

Fibres.	Iodine Solution.	Zinc Chloride + Iodine Solution.	Magnesium Chloride + Iodine Solution.
Mechanical wood pulp, jute, straw (partially boiled), unbleached manilla.	Yellow.	Yellow.	Yellow.
Cotton, linen, hemp . . . .	Brown.	Claret.	Reddish brown.
Esparto, straw, bamboo . . . .	Grey or greyish brown.	Blue to violet.	Bluish violet.
Wood cellulose . . . . .	Colourless.	Blue or violet.	Brownish or red.
Manilla hemp . . . . .	Yellowish brown or grey.	Yellow.	Yellow.

**Statistics.**—548,000 tons of paper, of value £6,410,000, were imported into the United Kingdom in 1910. The export was 144,000 tons, of value £3,140,000. The composition of the paper-making materials imported in 1910 is shown by the following figures:—

#### PAPER-MAKING MATERIALS IMPORTED INTO THE UNITED KINGDOM IN 1910

	Tons.	Value.
Linen and cotton rags . . . . .	18,500	£201,000
Esparto and other vegetable fibres . . . . .	193,000	666,000
Chemical wood pulp . . . . .	351,000	2,837,000
Mechanical wood pulp . . . . .	488,000	1,225,000
Other materials . . . . .	14,000	102,000

The United States in 1910 *imported* paper and paper manufactures to the value of \$3,390,000. The following figures give the *exports* :—

	1906.	1910.
Books, maps, printed matter -	\$5,839,000	\$7,089,000
Paperhangings - - - -	311,000	297,000
Playing cards - - - -	258,000	222,000
Printing paper - - - -	3,667,000	2,767,000
	(138,856,000 lbs.)	(92,738,000 lbs.)
Writing paper - - - -	\$976,000	\$1,267,000
All others - - - -	4,324,000	4,442,000

The paper-making materials *imported* into the United States is given by the following figures :—

	1910.	Value in 1910.
Rags - - - - -	180,114,000 lbs.	\$2,167,000
Wood pulp - - - - -	847,441,000 „	11,768,000
Other paper stock - - -	...	3,039,000

For modern statistics see Appendix III.

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## V.—MERCERISATION

### LITERATURE

“Mercerisation.” A practical and historical manual by *The Dyer and Calico Printer*. London, 1903.

GARDNER.—“Die Mercerisation der Baumwolle.” Berlin, 1898.

ICHENHÄUSER.—Article “Mercerisation” in Dammer’s “Chemische Technologie der Neuzeit.” Gives recent patents.

Cotton fibre when brought into contact with sodium hydrate solution containing more than 10 per cent.  $\text{Na}_2\text{O}$  changes from a hollow flattened riband to a thickened cylinder with practically no hollow. This effect is seen in cotton cloth as a shrinking in length and width accompanied by a thickening in substance, and is known as mercerisation, after the inventor Mercer (1844). Cloth so treated is stronger, and has an increased dyeing capacity. By acting on cloth weaved of a mixture of cotton and wool, the wool is unaffected, while the cotton shrinks up, causing a relief *crépon* effect.

Mercerisation is effected in two ways :—

1. The caustic soda (20-25 per cent.) is allowed to act on the cloth or yarn when stretched in frames, thus forcibly preventing any longitudinal shrinking of the fibres; the latter retain their original length and strength, but simultaneously acquire a beautiful silk-like lustre when the caustic soda is removed by washing.

2. The cotton is soaked in a solution of caustic soda, squeezed or centrifuged

F      E      D



FIG. 77.—Mather & Platt's Mercerising Range.

to get rid of excess of moisture, stretched a little beyond its original length, and washed while still in a state of tension to remove the NaOH.

Mather & Platt's apparatus for mercerisation is shown in the illustration (Fig. 77). The cotton fabric A first passes into the caustic soda tank B in the foreground, where it is twice soaked and twice squeezed dry by rollers placed inside; the goods then pass into the tension frame C, where it is stretched the proper amount, and afterwards in the second part of the apparatus D the caustic soda is removed by washing with warm water issuing from a central perforated pipe laid above the cloth, the wash water running away being caught and evaporated so as to regain the soda. On issuing from the tension frames the material passes in order through a washing-tank E, squeezing-rollers, an acid-tank, squeezing-rollers, and a couple of massive rollers F where it is strongly compressed; the cloth is then laid in folds as it issues from the machine. A section of Sir James Farmer's Mercerising Range is also shown in Fig. 78.

The strength of the cotton is increased by mercerisation 68 per cent. if unstretched, and 35 per cent. if stretched (Buntrock, *Z. Angew. Ch.*, 1898, 982).

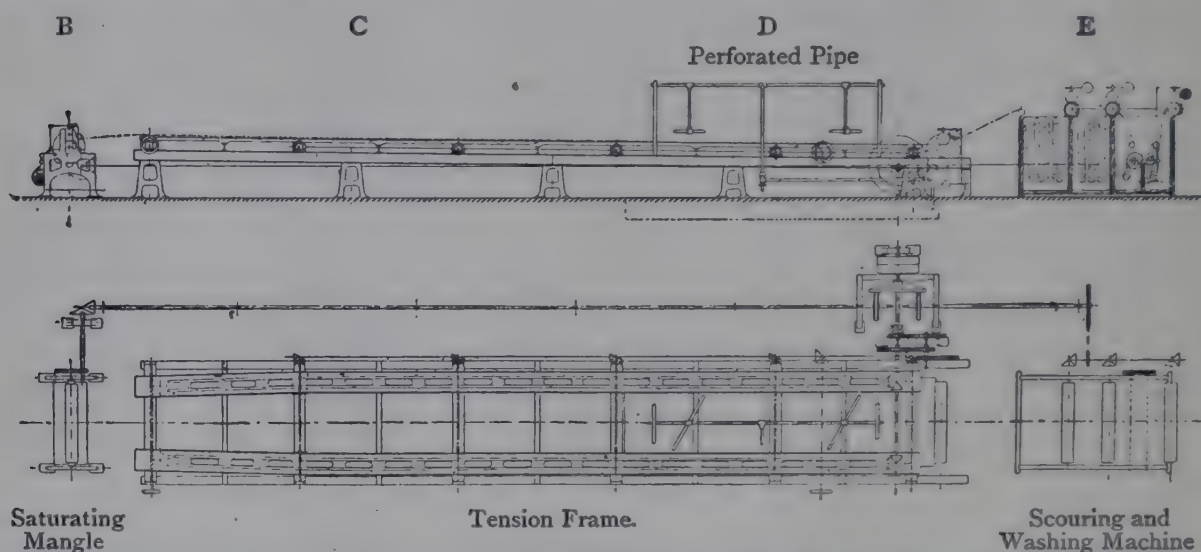


FIG. 78.—Section of Sir James Farmer & Sons' Mercerising Range.

The silky finish is especially marked when long-fibred sorts of cotton are employed, and is intensified by subjecting the mercerised material to a special calendering-process. Beautiful cr  pon effects are obtained by locally mercerising stretched cloth—the NaOH being prevented from spreading into neighbouring parts of the cloth by first printing the parts with gummy material; the caustic soda is then only able to mercerise those portions of the cloth not covered with gummy material. This process has now attained great industrial importance.

As far as the chemistry of the process is concerned it is thought that cellulose when treated with the NaOH forms the compound  $(C_6H_{10}O_5)_2Na_2O$ , which on washing decomposes into the cellulose hydrate  $(C_6H_{10}O_5)_2 \cdot H_2O$ .

**Tests.**—To distinguish between mercerised and non-mercerised cotton a microscopic examination is necessary. *Lange* advises treating the sample with a cold saturated solution of  $ZnCl_2 + KI + I$  (e.g., 30 g.  $ZnCl_2 + 5$  g.  $KI + 1$  g.  $I$  in 24 c.c. of water). Such a solution gives a *blue* colour to both mercerised and non-mercerised cotton. On rinsing with cold water the colour *persists* with *mercerised cotton*, and *disappears* with non-mercerised. If the cotton is coloured it must be bleached before applying the test.



## VI.—COLLODION

**Collodion** is a weakly nitrated cellulose, usually regarded as a dinitro cellulose,  $C_6H_8(NO_2)_2O_5$ ,\* containing 10-11 per cent. N, and easily soluble in a mixture of alcohol and ether (2 : 1). Several such dinitro-celluloses exist,† some soluble and some insoluble, and it is usual to distinguish between those intended for the manufacture of blasting-gelatine and nitroglycerin powder and those for making celluloid and for artificial silk. Usually the cotton wool is purified by treating with soda (wood cellulose requires such energetic purification that it is not used for the manufacture of nitro bodies), and then 1 part of cotton is nitrated with 20 parts  $H_2SO_4$  + 9 parts  $KNO_3$ . The cotton wool is left in the acid mixture until a sample, when withdrawn and crushed, will dissolve in a mixture of alcohol and ether (2 : 1). The temperature during nitration must remain low. The collodion wool (dinitro-cellulose) is washed with cold water, then with boiling water, and is carefully stabilised by heating when wet with dry superheated steam. The solution in alcohol-ether is also known as **Collodion**. It dries to a colourless elastic skin. Collodion is principally used in photography and medicine, for varnishes, films, and for impregnating incandescent mantles.

England imported 87 gals. in 1910, value £76. The United States in 1910 imported 84,500 lbs. (value \$335,900).

For modern statistics see Appendix III.

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\* On Eder's formula,  $C_{12}H_{16}(NO_2)_4O_{10}$  (tetranitrate), and on Vieille's,  $C_{24}H_{32}(NO_2)_8O_{20}$  (octonitrate); Vieille's more closely represents the facts.

† See p. 628.

## VII.—CELLULOID, XYLONITE, Etc.

## LITERATURE

- WORDEN.—“Nitro-cellulose Industry.” 2 vols. London, 1911.  
 MASSELON, ROBERTS, CILLARD.—“Le Celluloid.” Paris, 1910.  
 D. ERTEL.—“Die Celluloid Industrie.” 1909.  
 PIEST.—“Die Zellulose.” Stuttgart, 1910.  
 F. BOCKMANN.—“Celluloid.” London, 1907.  
 SCHMIDT.—“Papiermaché und Celluloid.” Leipzig, 1907.  
 ANDÉS.—“Celluloid.” Vienna, 1907.  
 BERSCH.—“Cellulose, Celluloid and Artificial Rubber.” London, 1904.  
 S. LEHNER.—“Die Imitationen.” Vienna and Leipzig, 1909. (Gives an account of the manufacture of imitations of tortoiseshell, coral, ivory, etc., from celluloid and similar bodies).  
*Moniteur Scientifique*, 1908, p. 648. Article on “Derivés Plastiques de la Cellulose et de les composes.”  
 See also under Celluloid Substitutes.

Celluloid consists of a low-nitrated cellulose, usually termed pyroxylin, and camphor, and was discovered by Alexander Parkes about 1860, and by the brothers Hyatt of Newark in 1869. These substances, when pressed together and warmed, unite to form a transparent substance, which is not explosive and which possesses properties very different from the component bodies. The nature of the union is unknown, but it is believed that a “solid solution” and not a definite compound is formed. Several processes exist for effecting the union, but they may be divided into two types:—

1. **The Dry Process.**—The well washed and dried pyroxylin is ground up as finely as possible under water in a Hollander (see **Paper-making**), the water is removed, and the mass is subjected to a very great pressure in a perforated vessel. Next, the mass is mixed with 40-50 per cent. of camphor, well kneaded and mixed in special machines and at the same time *colouring* matters and other products mixed in. The mass is now subjected to very great hydraulic pressure, and at the same time heated by steam to about 130° C. The nitrocellulose rapidly dissolves in the melted camphor, and celluloid is produced. After remaining in the press for some hours the celluloid is dried in a vacuum over  $\text{CaCl}_2$ . Hyatt's original method is a modification of this.

2. **The Wet Process.**—In the alcohol and ether process of Magnus & Co., 50 parts of pyroxylin are placed in stoneware vessels and 28 parts of camphor dissolved in 100 volumes of ether and 5 volumes of alcohol are added, and the whole, together with a “stabiliser” or “antacid,” such as urea, stirred up in the closed vessel (to prevent evaporation of the ether). The crude plastic stuff so obtained is rolled out into sheets, and after hardening is treated in a warm state in the hydraulic press. The process is only suitable for the production of moderately thin sheets or bars of celluloid. The danger of explosion and fire through the use of ether vapour is very considerable. Best uses methyl alcohol instead of ether for dissolving the camphor.

Celluloid is a horn-like, semi-transparent, or even transparent, body. It is hard, very tough, and elastic. Inferior qualities smell of camphor, the best sorts are odourless. It is insoluble in water, and when hot can be welded and moulded. At 125° C. it becomes plastic; at 140° C.-145° C. it decomposes without explosion. It is extremely inflammable, burning with a smoky flame, and emitting a camphor like smell. Celluloid cannot be made to explode by heating, friction, or a blow.



Since camphor is dear a large number of substances have been proposed in its place for making celluloid. Thus we may mention acetine, methyl naphthylketone, dinaphthylketone, naphthalene, naphthalene acetate, nitro-naphthalene, halogen derivatives of the aromatic hydrocarbons, esters of phenol, cresol, naphthol, etc. etc. The use of the carbonates of the phenols, cresols, and naphthols is suggested in the German Patent, 139,589; the use of borneol is suggested in the English Patent, 11,512, 1905. The English Patent, 5,280, 1904, suggests the use of mixed ketones, while the English Patents, 17,948, 1900, and 8,072, 1901, use the phenol ester of phosphoric acid.

The great disadvantage of celluloid is its inflammability, and many methods have been proposed for diminishing this, such as the addition of mineral fillers, such as asbestos, magnesium chloride, aluminium salts, etc. Organic compounds of silicon have been recommended (English Patent, 10,320, 1910) as fillers. It has also been proposed to use in place of the very inflammable nitrate other esters of cellulose. See next Section.

**Statistics.**—England imported celluloid ware to the value of £450,000 in 1910; xylonite and celluloid ware to the value of £167,000 were exported. The United States exported celluloid to the value of \$1,189,000 in 1910; \$341,000 in 1906.

For modern statistics see Appendix III.

(It is not possible to give a full account of this material, which is gradually being replaced by more modern plastics such as cellulose acetate, but the reader who requires a full article is referred to P. S. Adamson's monograph, published by the Plastics Institute.)

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## VIII.—CELLULOID SUBSTITUTES, ARTIFICIAL BONE, HORN, IVORY, AND SIMILAR PRODUCTS

### LITERATURE

See under works on Celluloid; also S. LEHNER, "Die Imitationen" (Vienna, 1909); J. HOFER, "Die Fabrikation künstlicher plastischen Massen" (Vienna, 1908); R. SCHERER, "Casein" (London, 1905); also an article in the *Moniteur Scientifique*, 1909, vols. 70-71, p. 157, "Etat Actuel de l'Industrie des Matière Plastiques Artificielles." For artificial Horn, Resins, and Shellacs see the *Journal of Industrial and Engineering Chemistry*, vol. i. (1909), pp. 149, 545; *Transactions of the American Electro-Chemical Society*, vol. xv. (1909), p. 597. See also Patent Specifications referred to in text below.

(a) From Cellulose Acetate, etc., non-inflammable celluloid substitutes are made by mixing cellulose acetate, formate, or double esters, such as the sulphacetates and phosphacetates (the latter being more readily soluble in cheap solvents), with camphor or its substitutes. The so-called "cellite" films for kinematographs are made in this way, and are only with difficulty inflammable. Combs, tovs, balls, etc., of this "cellite" are now manufactured and used as a substitute for the inflammable and even dangerous celluloid. (See English Patents, Nos. 26,075, 1901; 7,088, 1902; 1,441, 1910.)

Horn-like bodies are obtained from cellulose acetate by heating with mono- or polyhydric phenols, chloral hydrate, thymol and chloroform, castor oil and  $\text{CHCl}_3$ , or phenol alone under pressure (German Patents, 145,106, 151,918, 152,111; American Patents, 774,713 and 774,714; English Patent, 9,537, 1907).

Cellulose Formate is used in English Patent, 2,511, 1907, and Compound Cellulose esters in English Patents, 27,102, 1909; 8,646, 1910; 29,246, 1910. (See under Cellulose Esters for manufacture of cellulose acetate, etc.)

(b) From Casein or Milk Curds (see Industrial Casein, p. 79).

Galalith is the best known horn or celluloid-like substance obtained by the action of formaldehyde on casein (from milk). The casein is dissolved in alkalis (such as caustic soda or aqueous ammonia), and the clarified solution is precipitated with acids, filtered, pressed, and dried slowly during some weeks or months. The plates so obtained, when soaked in formaldehyde and dried, form a yellowish white translucent product, very tough like horn or ivory. It may be coloured or marbled by adding dyes, soot, cork powder, etc., to the casein solution before precipitation. Galalith has a sp. gr. 1.31-1.35, is moderately hard (2.5 Mohr), is a good electric insulator, can be cut and worked cold, and when warmed with water can be kneaded and moulded. It is practically non-inflammable. It cannot be obtained perfectly transparent, nor in leaves thinner than 2 mm. in thickness. Galalith is protected by the German Patents, 115,681, 127,942, 141,309, and 147,994. Analogous products are produced in various ways by Betz (English Patent, 14,319, 1906), Desgeorge and Lebreil (English Patent, 23,789, 1906), Goldsmith (English Patent, 412, 1909), Kathe (English Patent, 17,953, 1907), Schütze (13,601, 1909). (See also English Patent, 21,750, 1910.)

A somewhat similar product is made by dissolving dried casein in dil. NaOH solution, heating with sulphur, evaporating the clear liquid to a syrup, and adding water-glass or zinc and lead hydroxides, and, to increase the hardness, emery, sand, cork dust, wood meal, etc. etc. The product is cast into plates and dried. See German Patents, 153,228, 163,818, and French Patents, 367,407.



Celluloid-like bodies are obtained by mixing nitrocellulose and **casein**; also by treating a compound of casein with a metallic oxide (German Patents, 138,783, 139,905).

(c) **Aldehyde-Phenol Condensation Products (Artificial Resins, Bone Substitutes, etc.).**—When certain aldehydes, such as formaldehyde and phenols, are boiled together, condensation occurs, and resinous bodies are formed, which can be used in the manufacture of varnishes, or plastic masses for imitating horn, ebonite, etc.

A remarkable product called **Bakelite**, after its inventor, Baekeland, is manufactured by warming together equal weights of phenol and formaldehyde, and a small amount of an alkaline condensing agent. The mixture separates into two layers, the upper an aqueous solution, and the lower an intermediate condensation product called A. If this intermediate product be heated above 100° C., a final condensation product called C is obtained in a porous, spongy state, which may be avoided by proceeding under a pressure of 50-100 lbs. per square inch. The product is then a hard, solid mass called **Bakelite**. Bakelite (sp. gr. 1.25) is very hard, not elastic, and an excellent insulator of heat and electricity. Its price is lower than hard rubber, casein, celluloid, etc.

Wood, e.g., soft wood, may be soaked in the intermediate product A, and is then heated under pressure, whereby it becomes covered and impregnated with a brilliant coat of superior waxy varnish equal to the most expensive Japanese lacquer. With this coated soft wood results are obtained in making furniture which cannot be achieved even with the most expensive hard woods.

Cardboard, pulpboard, fibres, etc., when impregnated with A, on heating, produce a hard, polished material. It can be used for coating metallic surfaces; for replacing amber in pipe-stems; for buttons, billiard balls, knife handles, etc.; for compounding sawdust, wood pulp, emery, etc. etc. It is a very powerful cement, and can be used for making grindstones, bearings, etc.

A large number of condensation products of phenols and formaldehyde are producible, some of which are hard bodies, fusible, soluble in the usual solvents, forming substitutes for natural resins like shellac, etc., while others are hard, infusible, and insoluble substances, serving as substitutes for ebonite, celluloid, etc. Further information of these interesting products is given in *The Journal of Industrial and Engineering Chemistry*, vol. i. (1909), pp. 149, 545, *The Transactions of the American Electro-Chemical Society*, vol. xv. (1909), p. 597. (See also Patent Specifications (English), Nos. 1,921, 1,922, 2,122, and 21,566, A.D. 1908, and No. 8,875, A.D. 1905.)

The following notes on these interesting bodies will be useful. In 1871 Bayer showed that phenols and aldehyde react. Kleeberg in 1891, as the result of a violent action, obtained a hard irregular mass, insoluble and infusible, by allowing formaldehyde solution to act on phenol in the presence of HCl. Smith in 1899 moderated the violence of the action by solvents such as methyl or amyl alcohol; he also used acetaldehyde and paraldehyde, and finally evaporated, when a product was obtained which could be sawn, cut, and polished. Luft (1902) treats formaldehyde with phenol and acid in aqueous solution, and before the product has had time to harden he adds solvents such as glycerol, alcohol, or camphor. The product is similar to celluloid, but is less tough and flexible. Blumen (1902) adds an oxy-acid such as tartaric, and boils, thus producing a shellac substitute, which behaves like a soluble fusible natural resin. Fayolle in 1903 made a fusible **guttapercha substitute** by adding a large amount of glycerol to the  $H_2SO_4$  used for condensing the product. Story (1908) added 3 parts of 40 per cent. formaldehyde to 5 parts of 95 per cent. cresol or carbolic acid, boiled eight to ten hours, concentrated, poured into moulds and dried below 100° C. The product was infusible and insoluble. Speyer (1897) condensed naphthol or polyphenols (e.g., resorcin or pyrogallol) with excess of ammonia and formaldehyde, thus producing an antiseptic which slowly gives off formaldehyde. In 1907 F. Bayer & Co. produced a **shellac substitute** by using orthocresol. Grognot (1908) produced a shellac substitute in a similar manner, adding glycerol, and when the action is over distilling off the solvent. Helm in 1907 produced synthetic resins by using amines or ammonium salts as condensing agents. (The above is interesting historically, but for a more modern account see under **Plastics**.)

(d) **Horny substances (i.e., those containing keratine)**, such as claws, hoofs, horns, hair, etc., when cut up, dissolved in alkalis, precipitated by acids, pressed and treated with formaldehyde, form hard products like celluloid. (See German Patent, 134,314.)



## IX.—ARTIFICIAL SILK

## LITERATURE

- SÜVERN.—“Die künstliche Seide.” 2 Aufl. Berlin, 1907.  
 PIEST.—“Die Zellulose.” Stuttgart, 1910.  
 DR ICHENHÄUSER.—Dammer’s “Chemische Technologie der Neuzeit.” Bd. III., p. 27.  
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 W. P. DREAPER.—“The Artificial Silk Industry.” *Journ. Chem. Ind.*, 1909, 28, 1297.  
 CHAPLET ET ROUSSET.—“Les Soies artificielles.” (Paris, 1909); and “Le Mercerisage et les Machines à merceriser.”  
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 B. M. MARGOSCHE.—“Die Viskose.” Leipzig, 1906.  
 A. HERZOG.—“Die Unterscheidung der Natürlichen und Künstlichen Seiden.” Dresden, 1910.  
 MITCHEL AND PRIDEAUX.—“Textile Fibres.” London, 1910. (Gives the Patent literature.)  
 W. MASSOT. “Faser- u. Spinnstoffe.” *Z. Angew. Chem.*, 1912, 562.

Several methods are now successfully worked for dissolving cellulose and squirting the solution through fine orifices, so as to form fine, silk-like threads. The founder of the industry was Chardonnet, who first produced “collodion silk.”

(a) **Collodion Silk — The Cellulose Nitrate Process.** — Cellulose is treated with nitric acid, as in making gun-cotton, and thus converted into “collodion wool,” a weakly nitrated cellulose, containing 10-11 per cent. of N, in the form of two nitro-groups, thus,  $C_6H_8(NO_2)_2O_5$ . Wood cellulose cannot be used for making the nitrocellulose, since it does not yield a stable enough nitro-product. Cotton cellulose, boiled with soda and bleached with chloride of lime, is now universally used. The nitrocellulose is dissolved in about 6 parts of a mixture of alcohol and

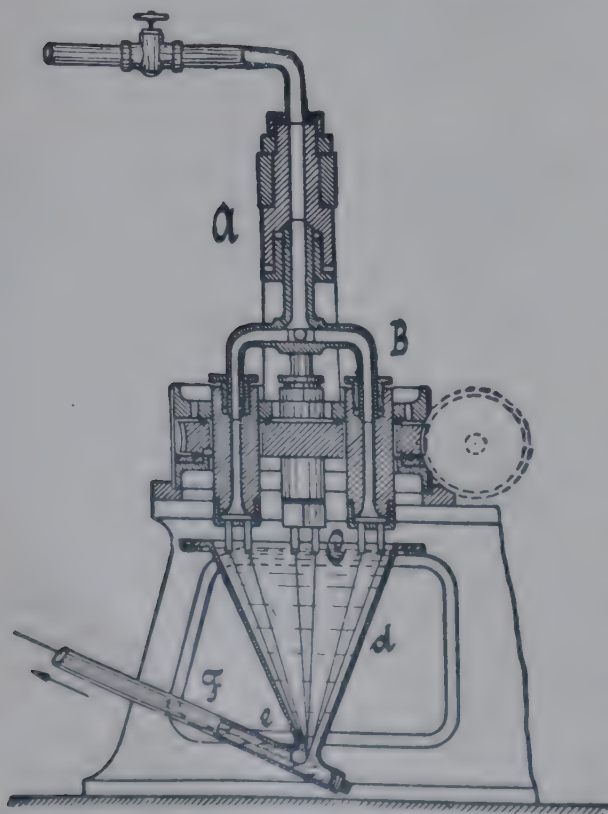


FIG. 79.—Collodion Silk—Wet Process.

ether (2 : 3) so as to form a thick syrup, which is carefully filtered and run into a tinned steel tank, where it is subjected to a pressure of about 50 atmospheres, and thus forced out in the form of very fine threads through a number of very fine glass tubes (*c*, Fig. 79), having openings of only 0.08 mm. diameter. According to the **wet process** the threads are spun out (squirted) — eight to thirty-six single threads simultaneously — into water, where they solidify and are continuously drawn off and twisted into a stouter single thread by a roller at *e*, Fig. 79. In the **dry process** of spinning (Chardonnet’s original process) the threads are forced out into a warm air chamber, where the alcohol and ether instantly evaporate, and the solid threads are drawn off and spun together (twisted) to form stouter threads, just as in the wet process. The alcohol and ether vapours are condensed, and so the solvents are recovered.



Both the wet and dry processes of spinning have their own peculiar advantages and disadvantages. In the wet process (Lehner) a 10 per cent. collodion solution is used, and the process of spinning is somewhat slow. In the dry process (Chardonnet) a 20 per cent. collodion solution is used, and the process is rapid, but complex machinery is required to condense the vapours of alcohol and ether. At the present time the greater part of the artificial silk is obtained by one or other of these processes.

The threads so obtained are explosive and very inflammable. They are, therefore, passed through a reducing bath, which removes the nitro-groups and reconverts the substance into non-explosive cellulose. To prevent explosion it is extremely important that the threads should contain not less than a certain percentage of moisture until the denitration has been effected. The reducing bath usually consists of a 10 per cent. solution of sodium sulphohydrate ( $\text{H}_2\text{S} + \text{NaOH}$  solution); sometimes calcium and magnesium sulphohydrates are also used. The nitrogen is reduced in a short time to 0.3 per cent., and the substance is now practically pure cellulose, being scarcely more inflammable than cotton. The denitrating process lessens the strength of the fibres, but increases their brilliance. The silk is well washed, bleached, washed, and dried.

The nitrocellulose process is a difficult and dangerous one. The nitrated cellulose is explosive, while alcohol and ether are very inflammable substances, giving vapours which seriously injure the health of the workmen. The chemicals used are expensive, and all the nitrogen used in the nitrating process is lost again in the denitrating process, and, indeed, up to the present is not recoverable. The great advantages of the process are: (1) the threads do not easily break in the winding and spinning process, so that there is little waste; (2) the collodion solution will keep indefinitely. In the other two processes to be described, the cellulose solutions are unstable and must be used soon after preparation. One of the great defects of the process has been the weakness of the threads after denitrating. Great improvements, however, have been effected in this direction. The gun-cotton product, however, is being slowly displaced by that prepared directly from cotton.

"Collodion silk" has been manufactured since 1891 in Chardonnet's large factory at Besançon. "Lehner silk" is a similar product manufactured in the Vereinigten Kunstseidefabriken in Frankfurt a. M. Enormous profits were made by some factories, and for a time the demand for the artificial brilliant silk was so great that its price actually rose for a time above that of real silk!

**(b) The Cuprammonium Process.**—This process depends upon the solubility of cellulose in a solution of copper hydroxide in ammonia.

The most important patents protecting the manufacture are those of *Pauly* (German Patent, 98,642, 1897); *Bronnert* (German Patent, 109,996, 1899); *Fremery and Urban* (German Patent, 111,313, 1899).

The cellulose is obtained from long-fibred cotton, purified by boiling with soda under 3 atmospheres pressure. The ammoniacal solution of copper is obtained (German Patent, 115,989) by charging an iron cylinder with copper turnings and adding a 20 per cent. ammonia solution and some NaOH solution ( $25^\circ \text{Bé.}$ ), while cold compressed air is driven into the solution. The temperature must not rise above  $4^\circ \text{C.}$  The solution should ultimately contain 45 g. of copper per litre, when it will take up 8 per cent. of cellulose. The solution must be as free as possible from inorganic salts. The percentage of cellulose dissolved increases with the percentage of copper present. The prepared cellulose is then mixed with the cuprammonium solution in special mixing or kneading machines, all contact with the air (and escape of ammoniacal fumes) being avoided. The solution is carefully filtered through fine metal cloth, so as to separate any undissolved fibres, and then forced through narrow orifices into a bath of sulphuric acid; the sulphuric acid removes the copper from the thread and gelatinises it; a 50 per cent. sulphuric acid is now used against a 10-20 per cent. formerly employed, as stronger threads of a higher lustre are obtained with the stronger acid. The individual threads are then spun together into thicker threads, consisting usually of eighteen single threads.

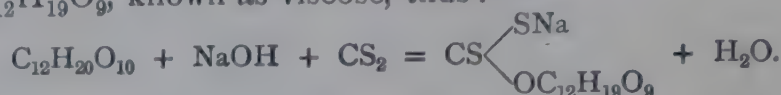
In order to remove completely all the copper, the threads are boiled with dilute acetic acid, washed with hot water, and dried on the spools (and therefore under tension) in a stream of warm air.

This variety of artificial silk is pure cellulose, and is sold under the names "Glanzstoff," "Sirius Silk," and "Meteor Silk." It is manufactured at Elberfeld (Vereinigte Glanzstofffabriken).



It is a strong product, possessing a very brilliant lustre, but with a somewhat feeble affinity for dyes.

(c) **The Viscose Process** (see also **Cellulose Solutions**, p. 188).—Cross and Bevan (English Patent, 8,700, 1892) dissolve cellulose by treating it with a concentrated solution of caustic soda, and then with carbon disulphide, as described on p. 189. The cellulose unites to form a water-soluble xanthogenate,  $\text{NaS—CS—OC}_{12}\text{H}_{19}\text{O}_9$ , known as viscose, thus:—



The solution is prepared in a kind of hollander, and is carefully filtered through porous cellulose plates, from which it passes directly to the final spinning-orifices. These are situated in the bottom of a thick-walled, air-tight vessel, which is connected to an air-compression plant. The spinning-orifices consist of conical glass tubes (sometimes provided with platinum jets) with exceedingly fine orifices.

The viscid solution is then spun into a solution of ammonium chloride which separates out the cellulose again, and gives the product known as “viscose silk.” Recently the spinning has been done in dil.  $\text{H}_2\text{SO}_4$  containing alkali sulphate or organic substances. The threads must be washed free from sulphur by passing through a series of washing solutions. The cellulose xanthogenate is unstable, being rapidly decomposed by acids, more slowly by water or ammonium chloride solution, into cellulose and a sodium sulphy-carbonate. The cheap wood-sulphite-cellulose can be used in this process; it appears to be the one most likely to supersede the others, since it yields a product equal or superior in strength and softness, and is cheaper and simpler than the Chardonnet or Pauly process. For improvements see *Stearn*, German Patent, 108,511; English Patent, 5,730, 1904; American Patent of *Waite*, No. 816,404, 1906, (which displaces the dear ammonium chloride solution for spinning into by sodium bisulphite solution); German Patent, 187,947, and A. 296, C. 16,663.

Eschaler (German Patent, 197,965) treats the fibres with formaldehyde, and states that they are thus rendered strong enough for making clothes.

(d) **Silk from Cellulose Acetate**.—The artificial silk produced by the three preceding methods consists of a modified form of cellulose, akin to mercerised cellulose, which absorbs more water from the air than normal cellulose, thus producing a cellulose hydrate. Another variety of artificial silk is made, however, which differs from the preceding in being, not cellulose, but cellulose acetate. The triacetate  $[\text{C}_6\text{H}_7(\text{C}_2\text{H}_3\text{O}_2)_3\text{O}_2]_n \cdot \text{H}_2\text{O}$  is often used, but other acetates are employed as well. For preparation and properties see under **Cellulose Esters**.

Cellulose acetate forms a horny mass, which dissolves in chloroform, glacial acetic acid, ethyl benzoate, and nitrobenzene, to form a thick, syrup-like solution, which may be squirted through holes into alcohol or ammonium chloride, so as to form fine, silk-like threads. Such “acetate silk” is considerably stronger and harder than cellulose artificial silk, and is non-inflammable, but has the disadvantage of being much dearer.

“Acetate silk” is an even better non-conductor of electricity than rubber or natural silk. An important commercial application is the coating of very fine copper wire for electrical purposes.

Formates of cellulose have also been proposed for making artificial silk (see p. 216).

### (e) Other Varieties of Artificial Silk

**Vandura or Gelatine Silk**, a very beautiful product, made from gelatine and formaldehyde, and having about the same percentage of nitrogen as natural silk, is too weak to be of much practical use. (See German Patent, 83,225.) Gelatinous silks, made from gelatine from sea-weed, Irish moss, agar-agar, etc. etc., have been proposed. (German Patent, 148,587.)

**Casein Silk**.—Casein dissolved in alkali or zinc chloride solution is forced into acid or other precipitating and hardening bath. (See German Patents, 170,051, Supp., 178,985, 182,574.) These



products up to the time of writing have attained little importance, but may ultimately do so when improved.

### (f) Coarse Artificial Fibres for Various Purposes

**Artificial Hair** has long been made by *Lehner* by the collodion process (which see, p. 212), by spinning out simultaneously several fine threads in such a manner that they meet while still in a soft condition, and then coalesce to a single thread of suitable dimensions. (See German Patent, 125,309.) The product is known as **Meteor Yarn** and **Sirius Yarn**, etc., used for cording in millinery. (Stout single threads squirted out from a large orifice of the proper dimensions are too weak to be of much use.) Instead of coalescing a number of fine threads, the German Patents, 129,420, 181,784, 186,766, and American Patent, 856,857, pass cellulose threads through solvents, which soften and partially dissolve the individual fibres of the thread, making them cohere together to a single homogeneous thick fibre, with a polished and smooth surface. The thread is then hardened.

If the artificial hair is to be used for making wigs, the lustre must be removed by various processes. (German Patents, 129,420 and 137,461.)

**Artificial Hemp Bast** may be prepared by mixing in zinc white, barium sulphate, chalk, etc., into a collodion, viscose, or other solution of cellulose, and then steeping fibres in the solution. (German Patent, 184,510.)

**Properties of Artificial Silk.**—Artificial silk possesses a more brilliant lustre than natural silk, and dyes well with cotton dyes, collodion silk even directly taking basic dyes. Artificial silk, however, has a much harsher feel than that of real silk; this is in consequence of the greater thickness of the threads, thus while real silk has a thickness of only 0.01-0.02 mm., the finest threads of artificial silk barely reach 0.03 mm. The reason of this is that up to the present it has been found impossible to make the openings in the glass spinning-tubes of a smaller diameter than 0.08 mm., although no doubt this difficulty will be overcome in time.

A more serious defect, however, is the want of strength, especially in a wet condition. In a dry condition the strength equals that of heavily weighted natural silk. The strength has been increased considerably of recent years, a toughening effect being produced by soaking in formaldehyde and similar chemicals (*e.g.*, see German Patents, 197,965, A: 296, C. 16,663). It has been found that the finer the fibres the stronger the woven cloth, and efforts have, especially in recent years, been made to spin finer and finer threads; on these lines the strength of natural silk may ultimately be attained or even exceeded.

**Uses of Artificial Silk.**—Artificial silk is used in large quantities for stockings, glittering braids and trimmings, and for relief on cotton cloths. Indeed for these purposes it is far better than real silk, since it gives excessive brightness to the fabric. It is also used in the form of **insertions** for ladies' blouses, ties, scarfs, and wearing apparel generally. Furniture stuffs and carpets are now beginning to be manufactured from it. Such artificial silk cloth is much more readily freed from dust than real silk cloth. Artificial silk, however, being much weaker than real silk (at least most of the kinds in use up to the present), is unsuitable for using in a pure state for making cloth. It is invariably used with other strong threads as backing.

This explains why the manufacture of artificial silk has not to any extent affected the volume of the trade in real silk, since it is used for a different purpose. About 25,000 tons of real silk are annually produced, while the output of artificial silk amounts from 5,000-7,000 tons yearly (1910). The English output was 270 tons in 1909. 1 kg. of artificial silk costs 15s. to 20s.; of real silk, 20s. to 40s. The introduction of artificial silk, however, in large amounts has had the effect of considerably lowering the prices paid for real silk, and should an artificial silk be ultimately produced having the mechanical strength and wearing properties of real silk, it may in time entirely displace it.

The English export of artificial silk amounted to £196,000 in 1910. The import amounted to £36,000. The United States imported 1,542,000 lbs. (value \$2,062,000) in 1910.

For modern statistics see Appendix III.

Artificial silk is also used for making artificial horse hair, hair for wigs, etc. Also for making incandescent lighting mantles, which are said to be very elastic and durable, with a longer and greater incandescent power than other kinds.



**Tests of Artificial Silk Yarns.**—Natural silk contains 17 per cent. of nitrogen. The various artificial silks contain from 0.07-0.16 per cent. N.

**Diphenylamine Sulphate** gives the following reactions:—

Silk	-	-	-	-	-	-	-	-	Brown coloration.
Tussah silk	-	-	-	-	-	-	-	-	„ intense.
Chardonnet and Lehner (nitrocellulose)	-	-	-	-	-	-	-	-	Intense blue.
Pauly, Viscose, or Yarmouth silks	-	-	-	-	-	-	-	-	No reaction.

A good method of distinguishing artificial silk from real silk or mercerised cotton is to heat the cloth to be tested for ten minutes to 200° C. Artificial silk is carbonised (though intact as regards structure) and falls to pieces on touching or rubbing, while real silk, cotton, or wool are hardly affected. Hence rubbing the heated and cooled cloth removes the artificial silk as dust, and by comparison with a piece of the original cloth the number of threads of artificial silk can be easily counted. Under the polarisation microscope dyed natural silk does not appear dichroic, while dyed artificial silks (of cellulose) are strongly dichroic if dyed with methylene blue, congo-red, or benzoazurine (Herzog).

## Cellulose Esters

**Literature.** W. MASSOT.—“Faser- u. Spinnstoffe.” *Z. Angew. Chem.*, 1912, 567.

**Cellulose Acetates.**—Several of these appear to exist, but according to Ost (*Zeit. f. Angew. Chem.*, 1906, S. 993) even the highly acetylated products, the so-called “Tetra-acetates,” are really Triacetylcelluloses,  $[C_6H_7(C_2H_3O)_3O_5]_n \cdot H_2O$  (disputed).

Lederer produces the triacetate by first treating cellulose with dilute acids, thereby converting it into hydrocellulose, and then acetylating with acetic anhydride and a very little concentrated  $H_2SO_4$  or glacial acetic acid, the process being carried out in the cold. (See English Patents, 11,749, 1900; 7,088 and 11,164, 1902; 734, 1903; 7,346 and 19,107, 1906; 3,103, 1907.) Another process directly acetylates the cellulose, which at the same time undergoes partial hydrolysis (Ost).

Cellulose acetate is also made on the industrial scale from cellulose regenerated from the sulpho-carbonate or viscose. Henckel-Donnersmonk's process consists in heating molecular proportions of cellulose and magnesium acetate with acetyl chloride, anhydrous acetic acid, and nitro-benzene.

It is soluble in chloroform, ethyl-benzoate, glacial acetic acid, and nitro-benzene, and is insoluble in methyl or ethyl alcohol, ethyl or amyl acetate, acetone, and ether.

It forms films of great transparency, is a better electric insulator than rubber or silk, and is non-inflammable. An important commercial application is the manufacture of “acetate” silk for coating very fine copper wire for electrical purposes (p. 214). Its price in 1910 was about thrice that of nitrocellulose.

Non-inflammable celluloid substitutes are made by mixing the less highly acetylated cellulose acetates with camphor. The so-called “**Cellite**” films for kinematographs are made in this way, and are only with difficulty inflammable. Combs, toys, balls, etc., of this “**cellite**” are now manufactured and used as a substitute for the highly inflammable and dangerous celluloid. See under **Celluloid**.

**Cellulose Formates** are made by acting on the cellulose with first sulphuric acid and then formic acid. A mixture of formates ensues which can be used for making artificial silk. (See English Patent, 17,036, 1909.) For an account of **other cellulose esters** see Piest, “Die Zellulose,” Stuttgart, 1910.

For esters of  $HNO_3$  see **Collodion**, p. 207.

Probably the most important artificial silk of recent years is nylon and its relatives. These are fully dealt with in Section XXII under **Plastics**.



# X.—NITRO-CELLULOSE LACQUERS, VARNISHES, DOPES

BY GEOFFREY MARTIN, Ph.D., D.Sc.

## LITERATURE

S. T. WORDEN.—“Nitro-Cellulose Industry.” New York, 1911.

Within recent years a large class of brilliant varnishes and enamels have been placed on the market, having as a basis soluble nitro-cellulose (or pyroxylin).

The main originators were John H. Stevens and O. P. Amend. (See United States Patents, 269,340, 269,341, 269,342, 269,343, 269,344, and 269,345. See Wilson and Storey, English Patent, 6,051, 1884; also United States Patents, 371,021, 372,100, and re-issue, 10,789, 1887.)

The first modern lacquer formula consisted of soluble nitro-cellulose (pyroxylin), 100 parts; amyl alcohol and amyl acetate, each 400 parts. Iso-propyl and iso-butyl and alcohols are also good solvents. Propyl and butyl acetates, and also amyl acetates, are the main solvents now employed.

A typical modern lacquer and corresponding diluting medium or thinner is:—

	Lacquer.	Thinner.
Amyl acetate - - - -	45 oz.	40 oz.
Pyroxylin - - - -	5.5 „	„
Refined fusel oil - - -	7 „	6 „
Wood alcohol (97 per cent.) - - -	24 „	35 „
Benzine (boiling point, 62°) - - -	32 „	20 „
„ ( „ 71°) - - - -	20 „	27 „

Hales' formula was amyl acetate, 4 gals.; benzine, 4 gals.; methyl alcohol, 2 gals.; and pyroxylin (soluble nitro-cellulose), 2.5 lbs.

Field's formula for a pyroxylin resin lacquer was:—

Amyl acetate - - - -	50 gals.
Spirits of turpentine - - - -	25 „
Methyl alcohol - - - -	25 „
Pyroxylin and shellac - - - -	37.5 lbs.

Crane's acetone oil lacquers consisted of:—

Volatile ketones (acetone oil, B.P., 100-140 centigrades) - - -	50 gals.
Wood alcohol - - - -	50 „
Pyroxylin - - - -	200 lbs.

He also used the following formula:—

Petroleum naphtha, or benzol - - - -	20 gals.
Volatile ketones - - - -	20-50 gals.
Wood alcohol or acetone - - - -	30-60 „
Pyroxylin - - - -	200 lbs.

The pyroxylin was dissolved in the acetone oil, and the other ingredients were added in any convenient order.

Ferner's formula for a thin and heavy lacquer consisted of:—

	Heavy.	Thin.
Nitro-cellulose - - - -	100 pts.	100 pts.
Amyl acetate - - - -	150 „	400 „
Amyl alcohol - - - -	150 „	400 „

Valenta uses 150 parts gun cotton in 1,000 parts acetone, and 2,000 parts each of amyl acetate and benzine. The liquid is clarified by decantation.

These lacquers may be rendered fire-proof by the addition of calcium chloride, triphenyl phosphate, and similar substances.

**Dip Lacquers** are colourless solutions of nitro-cellulose, containing six or seven ounces of solid matter to the gallon. Articles dipped in them become covered with an invisible coating of nitro-cellulose, which protects them from atmospheric oxidation.

**Pyroxylin Impregnation Paper.**—Printed matter, such as engravings, are often immersed in pyroxylin solution. They thereby become covered with a transparent varnish which preserves the print.

**Bronzing Lacquers.**—These consist of a nitro-cellulose solution which is used as a medium for the application of aluminium and bronze powder. Preparations are on the market under the names of bronzine, silverine, gold paint, etc.; large quantities are used in the picture frame industry. Most of these liquors contain amyl acetate, and about 2.75 oz. of nitro-cellulose per gallon. Sometimes resins amounting to  $\frac{1}{2}$ -1 $\frac{1}{2}$  oz. per gallon are added to the solution. Also copals such as kauri or manilla are added. A well-known liquid consists of 5 per



cent. celluloid, 45 per cent. amyl acetate, and 50 per cent. methylated spirit, to which 5 per cent. camphor oil has been added. The bronzing liquors are stirred into this.

**Coloured lacquers** can be made by stirring in aniline colours to the solvent. Such colours are auramine, chrysophenine, naphthol yellow, aurine, fuchsine, saffranine, vesuvin, magdala red, methylene blue, cyanin, Victoria blue, Bismarck brown, and for black spirits soluble nigrosines. Metallic colours are obtained by stirring in bronzing powders. **White enamels** are made by stirring in zinc oxide, carbonate, or sulphide into a solution of pyroxylin in amyl acetate, wood alcohol, camphor, fusel oil, and benzine.

**Heat-Resisting Bronzing Liquids.**—Steam pipes, radiators, and similar metal surfaces cannot be covered with a purely pyroxylin coating, as it soon peels off. Consequently for such surfaces a boiled linseed and other dry oils are added in the proportion of three to five ounces per gallon. Also resins are added—these are slow-drying preparations. The following are typical formulæ:—

	1.	2.		1.	2.
Amyl acetate - - -	40-50	35-45	Boiled linseed oil - - -	...	46
Fusel oil - - -	4-5	20-30	Pyroxylin - - -	2.75	3.0
Wood alcohol, 97 per cent.	35-50	15-25	Mastic or Canada balsam -	1.5	...
Benzine, 62 per cent. -	20-25	15-20	Copal - - -	...	4
„ 71° - - -	15-25	15-25	Aluminium powder or bronze	...	10

**Kerosene-soluble bronzing liquors** consist of 27 per cent. resin dissolved in 73 per cent. benzine (boiling point, 62°), with aluminium powder stirred in.

**Water-soluble bronzing liquids** are on the market, containing 27.5 per cent. sodium silicate. The aluminium powder and silicate are stirred together immediately before use. Such liquids are used for silvering cheap toys, picture frames, and interior plaster work of buildings.

**Methods of Using Nitro-Cellulose.**—All articles previous to the coating are well cleaned from dirt and grease, as for electroplating. The objects are then dipped into the lacquer which is contained in a tank. The articles are then drained at ordinary temperatures, and then are hung up in a drying room, preferably steam heated to about 45 degrees. The lacquer smooths itself in drying, and takes up its own drip. If upon drying the drip is not completely taken up, the lacquer is too heavy, and requires thinning.

**Preparation of Gilded Lace.**—Daly's process consists in first coating the lace with a collodion solution, then while moist, sprinkling the bronze over the surface. The excess of liquor is removed by a blower.

**Imitation Mother-of-Pearl Films.**—Hahn (English Patent, 13,139, 1894) dissolves 1 part nitro-cellulose in 78 parts 90 per cent. alcohol and 21 parts ether, and adds 5-10 parts of sodium silicate. This solution, when placed on wood or paper and allowed to evaporate slowly at ordinary temperature, gives a sheen and lustre like mother-of-pearl, caused by the silicate particles cracking up into a multitude of fine fissures.

Modifications of the process produce different colour effects. For example, potassium silicate and the addition of bronzing powders cause the appearance of fine colours. When fish scales or the dust on the wings of butterflies are dusted on the surface, very beautiful effects are stated to be produced. Finely powdered mica (made by mixing powdered mica with a 4 per cent. cellulose nitrate solution) produces a beautiful coloured bronze.

**Imitation Gold Leaf.**—Gregory (United States Patent, 826,781, 1906) dissolves a quarter pound of soluble nitro-cellulose in one gallon amyl acetate, and mixes with 25 per cent. bronze. After thorough mixing, the preparation is poured over a liquid heavier than the bronzing solution, such as water, carbon tetrachloride, or glycerine. The amyl acetate evaporates, and a thin metallic leaf is left on the surface of the water.

Silver leaf can be produced by substituting aluminium powder for the bronze.

This imitation gold leaf is stated to be sold as "Oriental Tissue," and "Japanese Leaf." It is stated that the above formula can be replaced by the cheaper solvent, amyl acetate, 45 per cent.; refined fusel oil, 8 per cent.; and benzine (boiling point, 52°), 47 per cent.

Kürtz (French Patent, 398,028, 1908) obtains gold leaf by mixing together nitro-cellulose, 26.25 parts; gold bronze, 20 parts; linseed oil, 3 parts; amyl acetate, 500 parts; benzine, 360 parts; and methyl alcohol, 45 parts. The mixture is spread out into thin sheets and dried.



## SECTION V

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### Fermentation Industries





# FERMENTATION INDUSTRIES

## I.—FERMENTS, ENZYMES, BACTERIA, MOULDS, YEASTS, ETC.

BY G. MARTIN, Ph.D., D.Sc.

With slight additions by E. I. COOKE, M.A.(Cantab.), B.Sc., A.R.I.C.

**Nature of Fermentation.**—Fermentation is the decomposition of complex organic material into substances of simpler composition by the agency either of protoplasm itself, or a secretion prepared by it (Green). Those agents which bring about fermentation are called “ferments.”

Most of the countless chemical changes which occur in the animal and vegetable kingdom—some of them of a truly wonderful nature—may be traced to the action of “ferments.” Such changes include processes of oxidation and reduction, putrefaction of organic matter, formation and splitting up of fats, ester formation, production of alcohol from sugar, etc. etc.

Many of the oldest industries in the world's history—the making of wine, beer, and vinegar, the souring and clotting of milk to form cheese, the tanning of hides—are dependent upon the action of ferments to which bacteria and other organisms or living tissues give rise. The same is also true of the fermentation processes employed in the extraction of natural indigo, in the preparation of coffee and cocoa, in the curing of tea and tobacco, and in the retting of flax.

So far as technical chemistry is concerned, the most important “ferments” are those which cause the generation of alcohol from sugar and starch, and to which we owe the enormous alcoholic industries of to-day. Before giving particulars of alcoholic fermentation, we deem it advisable to give a brief survey of the other ferments, referring the reader for further information to the very numerous standard works on the subject, a list of which is given below.

For our purpose “ferments” may be divided into two classes:—

- A. Unorganised Ferments or Enzymes.
- B. Organised Ferments.

### A. THE ENZYMES OR UNORGANISED FERMENTS

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 HARDEN AND YOUNG.—“The Alcoholic Ferment of Yeast-Juice,” *Roy. Soc. Proc., B.*, 77 (1906), 405; 78 (1906), 369; 80 (1908), 299; 81 (1909), 336.  
 HARDEN.—“Alcoholic Fermentation.” London, 1911.  
 H. EULER.—“Allgemeine chemie der Enzyme.” Wiesbaden, 1910.  
 H. LLOYD HIND.—“Brewing, Science and Practice,” vols. i. and ii. Chapman & Hall, 1943.

Enzymes are complex nitrogenous substances of exceedingly high molecular weight and similar in elementary composition to the albuminous substances. They are soluble in cold water, forming very slightly diffusible solutions, from which they may be precipitated by alcohol or ammonium sulphate as a white amorphous powder. In solution their chemical activities are weakened at 60° C., while a temperature of 80° C. usually destroys them. When dried, however, they will often stand considerably higher temperatures. Their aqueous solutions rapidly



putrefy. In glycerol, however (in which they are soluble), they may be preserved for a considerable time. Antiseptics and strong mineral poisons, such as formaldehyde, phenol, strong mineral acids or bases, lead, copper, mercury or zinc salts, potassium cyanide, etc., destroy enzymes. Enzymes possess the remarkable property of attacking complex organic molecules, splitting them up or "hydrolysing" them into simpler substances, usually with the addition of water. They thus render soluble substances like starch, fats, albumen, etc.

A similar hydrolysing action is caused by mineral acids or bases, or superheated water, and, according to Professor W. Ostwald, the enzymes merely accelerate actions which could occur, although slowly, under normal conditions even without the presence of an enzyme. The enzymes are thus regarded as "contact substances," as they themselves undergo but little change, a very small quantity of an enzyme being capable of hydrolysing enormous quantities of material. In certain cases ferments can also effect a synthetic process. Thus Croft Hill has been able to produce isomaltose by the action of the enzyme maltase upon dextrose:  $2C_6H_{12}O_6 = C_{12}H_{22}O_{11} + H_2O$ . Emil Fischer and his co-workers have synthesised certain decomposition products of albumen by means of enzyme action, while Kastel and Loevenhart have synthesised ethyl butyrate by bringing together ethyl alcohol and butyric acid in the presence of the fat-splitting enzyme lipase. The researches of Croft Hill, Kastel and Loevenhart, etc., show that enzyme action is in many cases reversible.

The enzymes are very widely distributed in the living world, both animal and vegetable, occurring in the saliva, in the gastric juices, in the pancreas, kidneys, blood serum, and plant juices. By their aid the foodstuffs are rendered soluble and digested. The enzymes are produced directly by *living* protoplasm cells from albumen and similar substances; once formed they may, as stated above, be removed from the plant or animal, and retain their activity for a considerable time.

Each enzyme is characterised by its capacity of performing **one specific chemical action**, and they are most easily classified according to the actions they perform.\* Thus we have:—

1. **Diastatic Enzymes**, which dissolve insoluble carbohydrates like starch and cellulose, converting them into soluble sugars.

The best known and most important vegetable enzyme is **amylase (diastase)**, which occurs in **malt** (germinating barley) and other germinating seeds, and in many fungi. It occurs only in traces in the raw corn grain itself, but develops rapidly when the grain begins to germinate.

It may be obtained by extracting green malt with cold water, and precipitating with alcohol or ammonium sulphate. It then forms an amorphous powder which is purified by repeatedly redissolving and reprecipitating, and by subjecting to dialyses. The product thus obtained possesses a varying composition, those preparations being most active in which the elementary composition (especially the nitrogen) approximates most closely to albumen. Thus we may get

C	-	-	-	-	44.52 per cent.	S	-	-	-	-	1.2 per cent.
H	-	-	-	-	7.66 "	O	-	-	-	-	33.23 "
N	-	-	-	-	9.16 "	Ash	-	-	-	-	5.6 "

Vegetable diastase rapidly dissolves starch, producing **maltose**; the optimum temperature is  $40^{\circ}$ - $60^{\circ}$  C.; at  $80^{\circ}$  C. it becomes inactive and coagulates. In a dry condition it can stand a temperature of  $150^{\circ}$  C., becoming inactive at  $158^{\circ}$  (Hueppe).

Ordinary **vegetable diastase** is undoubtedly a mixture of several distinct enzymes. One of these hydrolyses the starch to **dextrines**, and then stops its action. Another hydrolyses the **dextrines** to **maltose**.

It should be noted that ordinary malt contains in addition to diastase also ferments like **glucose** (maltase), **invertase**, and **proteolytic ferments** (see below).

**Saliva diastase** (ptyalin) in saliva and **pancreas diastase** (amylase) behave similarly to vegetable diastase, but are apparently not identical with it. **Inulase** decomposes inulin; **cytase** or **cellulase** dissolves cellulose, destroying cell-walls and thus allowing diastase to attack the enclosed starch.

\* The nomenclature now generally adopted is to denote each enzyme by the name of the substance it especially attacks, with the addition of the suffix "ase," e.g., **maltase** is the enzyme which decomposes maltose, **cellulase** that which decomposes cellulose.



**2. Inverting Enzymes.**—These transform sugars of the biose type (disaccharides) into simpler sugars, usually hexoses.

**Invertase** or **Sucrase** hydrolyses cane-sugar into *d*-glucose and *d*-fructose; most rapidly at 55°-60° C. It is inactive at 75° C. It is contained in yeast cells, and may be obtained from them by drying at 105° C., extracting with water, and precipitating with alcohol; also contained in **malt**. Easily soluble in water and diffusible, and acts only in acid solution. May be heated when dry for one hour at 140°-150° C.

**Maltase** or **Glucose** converts maltose into 2 molecules of glucose; occurs in malt and in many culture yeasts. Is difficultly soluble in water and can only be extracted from crushed and ground cells by leeching. Optimum temperature, 40° C. Destroyed at 50°-55° C.

**Lactase** converts milk sugar (lactose) into *d*-glucose and *d*-galactose; occurs in milk sugar yeasts (S. Kefir) and some culture yeasts, never in brewing culture yeast. Does not diffuse or penetrate the cell wall.

**Melibiose**, which is present in some bottom-fermentation yeasts and absent from most top-fermentation yeasts, splits melibiose into *d*-glucose and *d*-galactose. Obtained by leeching dried cells with water; cell diffusible.

**Trehalase** splits trehalose, not diffusing.

**3. Ferments which decompose Glucosides.**—**Emulsin**, contained in bitter almonds, decomposes the glucoside amygdalin into grape sugar, benzaldehyde, and hydrocyanic acid. **Myrosinase**, the ferment of **black mustard seed**.

**4. Proteolytic Enzymes.**—These decompose the various soluble and insoluble proteid substances (such as albumen, fibrin, etc.) into simpler bodies, such as peptone, etc., sometimes decomposing them into simple amido-acids, such as leucin, tyrosin, aspartic acid, etc.

Among these enzymes we may mention the **pepsin** of the mucous membrane of the stomach, which decomposes albuminous bodies into **peptones**, and is most active in the presence of 0.02-0.04 per cent. free HCl; **trypsin**, the proteolytic ferment of the **pancreas**, which decomposes albuminous substances into leucin, tyrosin, and other amido-acids; **papain**, of the papaw tree, acts on flesh.

**Yeast Endotryptase.**—Optimum action occurs in 0.2 per cent. of HCl; optimum temperature, 40°-45° C., destroyed at 60° C.; retains efficiency in yeast juice nine to fifteen days at 37° C., and converts yeast albumen into tyrosin, leucin, xanthine bodies, and passive albumoses, but not into peptones.

**5. Clotting Enzymes, e.g., rennet (lab, chymosin)**, which coagulates milk precipitating the casein, but leaving the milk sugar in solution. Prepared from stomach of calf by macerating with water. Also occurs in **yeast cells**. Destroyed at 65° C. (two hours); non-diasable. **Thrombase**, which coagulates blood; **pectase**, which produces vegetable jellies.

**6. The Lipases**, which split up fats into glycerin and fatty acids. Occurs in the **pancreas**, also in various seeds, especially in castor seed. (See p. 93.)

**7. Oxidases**, which oxidise various substances, *e.g.*, **laccase**, **tyrosinase**. **Oxydase** and **cutalase** occur in yeast cells.

**8. Enzymes**, which decompose **amides, e.g., urase** in urine, which splits up urea into CO<sub>2</sub> and NH<sub>3</sub>.

**9. Alcohol Producing Enzymes, e.g., Buchner's zymase**, secreted by yeast cells, which decomposes grape sugar, etc., directly into alcohol and CO<sub>2</sub>.

Zymase will not pass through the yeast-cell wall and hence can only be isolated by breaking down the cell wall. This Buchner effected in 1897 by grinding up the living yeast cells with quartz sand and kieselguhr (infusorial earth) and then pressing out the juice in a filter press under a pressure of 400-500 atmospheres. The clear opalescent fluid rapidly ferments cane sugar, grape sugar, and fructose, but not lactose or mannitol. The action is not stopped by chloroform nor by passage



of the liquid through a Berkefeld filter, or dialysing membrane. The fermentation is a true alcoholic one, in that alcohol and  $\text{CO}_2$  are produced in the same proportion as when living yeast is used. The same by-products—such as glycerol and succinic acid—are also produced.

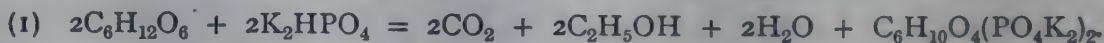
Zymase may be precipitated by alcohol-ether or acetone from its aqueous solution, and after drying is obtained as a white amorphous powder, which (even after prolonged keeping) when redissolved in water does not lose its fermentative power.

It does not appear to be sensitive to the action of dry heat up to  $100^\circ \text{C}$ ., since yeast thus killed still contains the active ferment. Büchner's expressed yeast juice rapidly loses its alcohol-producing power on standing, the zymase being destroyed by another enzyme, which is capable of digesting albumen, namely, a proteolytic enzyme called **endotryptase**, which also causes the auto-digestion of yeast cells. The destruction occurs most rapidly at  $40^\circ\text{--}50^\circ \text{C}$ .

R. Albert prepares his **zymin** or **permanent yeast** (*Dauerhefe*) by partially drying ordinary yeast, immersing in ten times its volume of acetone for fifteen minutes (which kills the living yeast), drying on filter paper, and well washing with ether, finally drying at  $45^\circ \text{C}$ . The white powder so obtained contains only **dead yeast** cells (with cell walls intact), and contains the **zymase ferment** uninjured. Consequently it will bring about vigorous fermentation, even after keeping for years.

Albert's process is interesting because yeast cells which have died in the ordinary way will not yield a juice capable of fermenting sugar. This only occurs when the cells are killed by acetone or alcohol (as above described), which at the same time acts as a preservative on the zymase ferment in the cell. It should be noticed that **zymase** certainly consists of several enzymes. Harden and Young have shown that when Büchner's yeast juice is forced through a Martin filter it is separated into two parts, namely, a residue (colloidal and non-diasable), which remains behind, and a liquid, which passes through the filter. Neither this residue nor the liquid which passes through are separately capable of causing alcoholic fermentation. On mixing them, however, a vigorous alcoholic fermentation is produced. Hence the alcoholic fermentation is due (1) to a colloidal, (2) to a crystalloidal substance.

Harden and Young have shown that phosphoric acid is one necessary constituent of the dialysable (crystalloidal) substance taking part in the fermentative action. For every molecule of sugar which is broken down into alcohol and  $\text{CO}_2$ , a molecule of a complex hexose phosphate (a compound of a sugar molecule with two of phosphate) is simultaneously formed, and this phosphate passes repeatedly through the cycle of changes represented in the following equations:—



The rate of fermentation by yeast cells and the factors governing it have been exhaustively studied by Arthur Slator and H. J. S. Sand, see p. 239.

## B. ORGANISED FERMENTS

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The chemical changes involved in the processes of alcoholic fermentation and in the putrefaction and decay of organic matter are due to the presence of minute organisms, which for convenience we group under the name "organised ferments."

It was once thought that these chemical changes were brought about by the direct action of the living protoplasm of these organisms. It is now, however, almost universally believed that these minute organisms *secrete* enzymes, which by their "contact" action bring about the various changes, and consequently that all such changes in reality are a direct consequence of unorganised ferments or enzymes.

The micro-organisms whose chemical activities are thus grouped under the general name of "Fermentation" are minute chlorophyll-free **plants**, belonging to the great family of "**Fungi**." So far as the fermentation industries are concerned, they may be divided into three groups: (1) **Bacteria**, (2) **Moulds**, (3) **Yeasts**.

### Bacteria (Schizomycetes)

**Bacteria** are the lowest forms of vegetable life, and the smallest living organisms that we are acquainted with, often requiring a magnification of over 300 diameters before becoming visible. They multiply either by splitting into two (*i.e.* by **fission** or cell-division—hence their classification among the fission-fungi and their name **schizomycetes**) or by **spore-formation**, *i.e.*, by the production of small protuberances, which eventually separate from the main organisation. These spores are often extraordinarily resistant towards heat, cold, want of nutrition, and even poisons. They germinate under favourable conditions into organisms similar to the parent organisms. **Bacteria** are colourless

(devoid of chlorophyll) plants and possess an envelope or capsule consisting of cellulose or allied substances. They are monocellular organisms, existing as—

1. Round cells (*coccaceæ*), often less than 0.001 mm. diameter.
2. Rods (*bacteriaceæ*), sometimes united into long **threads**.
3. *Leptotricheæ* } higher bacteria.
4. *Cladotricheæ* }

They are often provided with delicate threads—**flagella** or cilia—which serve as locomotive organs.

**Bacteria** are very widely distributed in nature. In unnumbered millions they occur in the air, soil, and water. On account of their minuteness they are rapidly transported by the wind and blowing dust from place to place. Wherever food is plentiful they develop enormously, and thus it is that all dead plants and animals are rapidly consumed by them, undergoing, as the result of bacterial vital activity, the familiar phenomena of putrefaction and decay. Their most important function is the breaking down of complex organic substances into simple inorganic compounds, which are again available for plant nutrition.

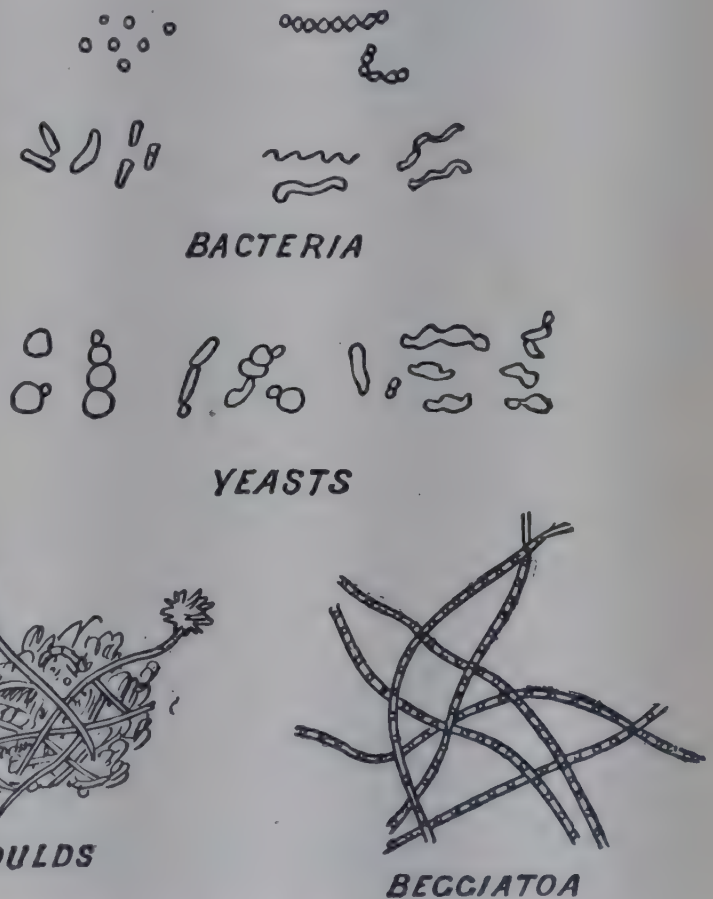


FIG. 80.—Bacteria, Yeasts, Moulds, and Beggiatoa.



Certain bacteria produce strong poisons as the result of their vital activity. For example, the **ptomaines**, or alkaloids of decay, which are found in putrefying flesh. Others are capable of producing chemical changes in the bodies of higher living organisms, and in the case of specific diseases—(caused by “pathogenic” bacteria), such as cholera, typhus, diphtheria, etc.—generate poisons (toxins), which are the direct cause of the illness. Artificial cultures of these bacteria also produce those poisons which, if injected into an animal, set up the same symptoms of disease as if produced by the multiplication of the microbes within the animal. To defend themselves against such bacterial poisons, animals produce in their serum antidotal poisons known as “anti-toxins”—which are probably enzymes—and use is made in Medicine of this fact in the curative treatment of

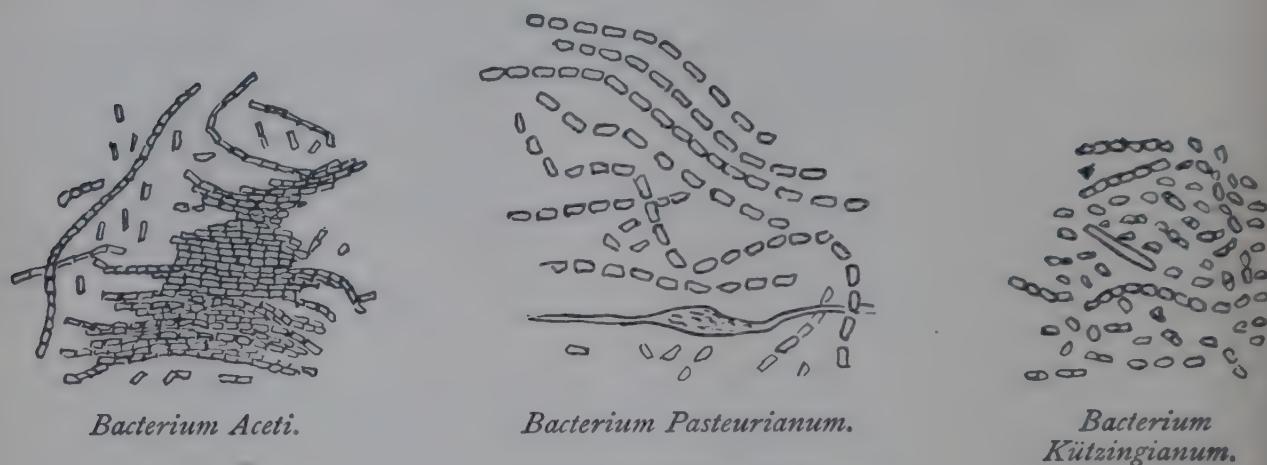


FIG. 81.—Acetic Acid Bacteria (Hansen).

disease. Thus the Farbwerke Höchst manufacture an anti-toxin from the serum of horse blood, which when injected into a patient cures diphtheria. Similar inoculating serums are used in the treatment of plague and other diseases. Bacteria require as food certain mineral and organic material. Many require oxygen, while some are killed by it (“anærobic bacteria”), others can develop both in the presence and in the absence of oxygen. There are innumerable races of bacteria—quite as definite in character as animals or plants—and pure cultures of the individual races are made by methods in vogue in bacteriological technique, for an account of which the reader is referred to one of the special text-books dealing with the subject. See also **Yeast**.

Most bacteria are destroyed by antiseptics. They are also usually killed by steam at  $100^{\circ}\text{C}$ .; they are almost instantaneously killed by high-pressure steam.

The following varieties of bacteria are of great use in the chemical industry:—



FIG. 82.—Lactic Acid Bacteria in Sour Milk.  
(*Bacillus Bulgaricus*.)

**Acetic Acid Bacteria.**—These cause the oxidation of alcohol into acetic acid, thus:  $\text{CH}_3\cdot\text{CH}_2\text{OH} + 2\text{O} = \text{CH}_3\cdot\text{COOH} + \text{H}_2\text{O}$ . Several varieties exist, such as *Bacterium aceti*, *Bacterium Pasteurianum*, *Bacterium Kützingianum*, and *Bacterium xylinum*, etc. They grow in dilute alcoholic fluids (containing under 10 per cent. alcohol), such as wine and beer, which contain the mineral and nitrogenous matter necessary for their nutrition. Continental varieties develop best at  $30^{\circ}\text{--}35^{\circ}\text{C}$ ., and require oxygen. According to Mitchell (see **Vinegar**)

English varieties flourish at  $40^{\circ}\text{--}43^{\circ}\text{C}$ . As the result of their activity, a thick skin—known as the **vinegar plant**, or “mother of vinegar”—covers the surface of the fermenting liquid, sometimes to the depth of 1 in. It is formed of the extensively developed mucinous envelope of the cells, and consists principally of cellulose. The bacteria occur as short rods, 0.001–0.003 mm. in length, often attached together in chains by their mucinous envelope. They occur widely distributed in fermenting liquids wherever there is plenty of air. They are used technically for the manufacture of vinegar (which see, p. 315).



**Lactic Acid Bacteria.**—These split up sugar into lactic acid, thus:  $C_6H_{12}O_6 = 2C_2H_4(OH).COOH$ , and are the cause of the souring of milk. Their optimum temperature is  $30^{\circ}$ – $50^{\circ}$  C., and being capable of developing at  $50^{\circ}$  C.—a temperature unfavourable for most other organisms—can easily be obtained as pure cultures. They occur on fruit, corn grains, malt, etc., and are cultivated extensively for the manufacture of **Lactic Acid** (which see, p. 317).

**Butyric Acid Bacteria** ferments lactic acid (and, it is stated, sugar and other carbohydrates) directly into normal butyric acid, the change being accompanied by the evolution of  $CO_2$  and  $H_2$ , thus:  $2C_3H_6O_3 = C_3H_7.COOH + 2CO_2 + 2H_2$ .

Many varieties of these bacteria exist, occurring on fruit, and causing the souring of cut beet, spent malt, distillers' wash, etc., the ripening of cheese, the rotting of wet potatoes, and the retting of flax. Certain kinds (e.g., *B. amylobacter*) dissolve cellulose. In the brewing industries the presence of butyric acid bacteria may cause great damage. The best known variety is the *Bacillus butyricus*, which consists of thin, motile rods, having an optimum temperature of  $40^{\circ}$  C., and flourishing in the absence of oxygen. (See **Butyric Acid**, p. 320.)

**Proteolytic Bacteria** are used in the tannery in the "bating" or "puering" process. These bacteria produce digestive enzymes which have a solvent action on the fibres of the skin, rendering it more supple. They have been studied and described by Mr J. T. Wood (see *Journ. Soc. Chem. Ind.*, 1910, **29**, 666), who has successfully made use of a puer-substitute called "erodin" which consists of a culture medium of peptonised gelatinous tissue, with a special mixed culture of selected bacteria (see pp. 580, 581).

**Nitrogen-fixing Bacteria.**—A number of bacteria exist in the soil, which cause the gradual fixation of atmospheric nitrogen, the oxidation of ammonia to nitrites, and of nitrites to nitrates. They are of the greatest importance to agriculturists. Two well-defined organisms convert **ammonia** into nitrites, viz., **nitrosomonas** and **nitrosococcus**. The **nitric** organism, which oxidises the nitrites to nitrates, is a very small bacterium.

Other bacteria are used technically in the dairy, in the preparation of indigo, tobacco, tea, etc., and especially in the modern method of sewage disposal, where the noxious substances are completely oxidised to  $CO_2$ , water, etc., by special bacteria cultivated in the filter beds. **Sulphur** bacteria exist which absorb  $H_2S$  and other sulphur-containing compounds, oxidising them to sulphates. A. Fernbach (pp. 314, 333) has produced cultures which give *fusel oils* (butyl alcohol) and *acetone*.

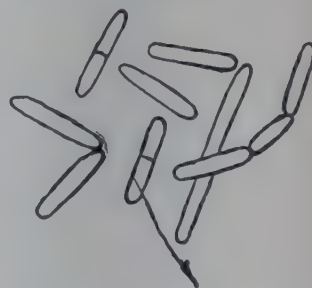


FIG. 83.—Butyric Acid Bacteria.

### Moulds (Hyphomycetes).

These are more highly organised than bacteria or yeasts; they propagate from **spores** (conidia), which develop into long threads of cylindrical cells forming a network known as **mycelia**. From these cells special seed-bearing organs—the **hyphæ** or **thalli**—develop. The moulds derive their names from these organs.

Moulds readily develop in sugar solutions, on moist bread, fruit, moist corn grains, wood, and even on damp walls. They act both as oxidising and hydrolysing ferments, and are, as a rule, not harmful.

Among the more widely distributed moulds may be mentioned: *Penicillium glaucum*, a green mould; *Aspergillus glaucus*, likewise green; *Aspergillus niger*, which appears dark. All these oxidise **sugar**, generating organic acids. They also contain enzymes, which hydrolyse **starch** and **albumen**. Two kinds of moulds—*Citro-mycetes*—are known which oxidise sugar (up to 50 per cent.) into **citric acid** in the presence of  $CaCO_3$ , and have been used technically for that purpose, but up to the present without success (see **Citric Acid**, p. 374).

Two moulds, *Aspergillus Oryzae* (Japan) and *Mucor (amylomyces) Rouxii* (China), grow on rice, and are used for making **saké** (rice beer) and **arrak** from rice (in the same way that we use **malt** for making beer from corn grains), since they contain **diastase** (or a similar enzyme), which hydro-



lyses rice starch into **fermentable sugars**. They have been employed for this purpose in Europe (see **Amylo Process**, pp. 286, 249). The mould *Mucos racemosus* splits sugar into alcohol and  $\text{CO}_2$ .

### Yeasts (*Saccharomycetes*)

The yeasts are single-cell fungi, more highly developed than bacteria, but less developed than moulds. They propagate by the formation of small daughter cells or buds, which are extruded from the parent cell—hence their name “budding fungi.” Some yeast fungi have been observed to propagate by fission. Many species form endospores under special conditions, while other species do not possess this capacity. Yeasts will only develop in media containing sufficient nitrogenous and mineral food for their nutrition.

**Alcoholic Fermentation.**—Yeast fungi decompose sugar into alcohol and carbon dioxide, according to the equation:  $\text{C}_6\text{H}_{12}\text{O}_6 = 2\text{C}_2\text{H}_5\text{OH} + 2\text{CO}_2$ . The monosaccharides (hexoses)—dextrose, laevulose, mannose, galactose—are thus decomposed by all true yeasts. The disaccharides—cane sugar and maltose—are not directly fermented in this manner, but have first to be hydrolysed into monosaccharides by enzymes contained in the yeast. **Milk sugar** is only fermented by a few yeasts which contain the enzyme **lactase**. Most yeasts do not contain

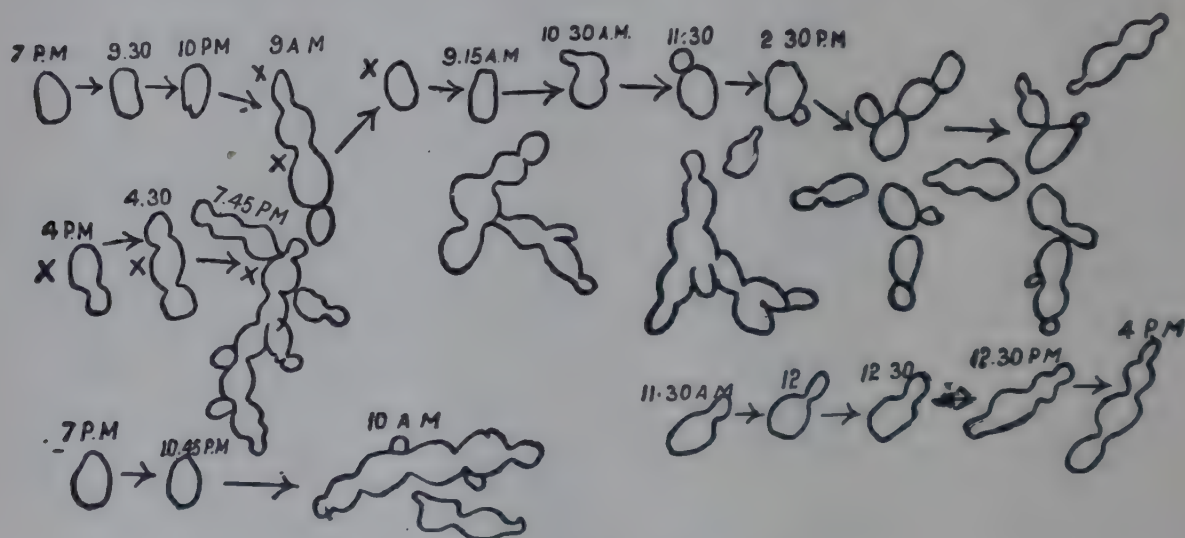


FIG. 84.—Budding Yeast.  $\times 600$ .

enzymes which hydrolyse **starch** and **cellulose**, and hence these substances have to be converted into sugars by **diastase** (*e.g.*, in malt) before yeasts can ferment them into alcohol. See p. 239 for **Rate of Alcoholic Fermentation**.

Only about 95 per cent. of sugar is transformed by alcoholic fermentation into  $\text{CO}_2$  and alcohol, for about 5 per cent. of by-products—such as glycerol, succinic acid, fusel oils, and higher alcohols—are produced as the result of the vital activity of the yeast cells. Thus, according to Pasteur, 100 parts of glucose yield on fermentation :—

Alcohol	-	-	-	-	-	-	-	48.4
$\text{CO}_2$	-	-	-	-	-	-	-	46.6
Glycerol	-	-	-	-	-	-	-	3.3
Succinic acid	-	-	-	-	-	-	-	0.6
Fusel oils and cellulose	-	-	-	-	-	-	-	1.1
								100.0

It is traces of these by-products which give a characteristic taste and smell to different alcoholic liquors. From grape juice (must) we get the scent “wine oils” which give a “bouquet” to the wine. Potato starch yields unpleasant smelling “fusel oils.” See pp. 251, 298, 314.

A. Fernbach has obtained cultures which produce *fusel oils* and *acetone* (see pp. 314, 333).

**Enzymes contained in Yeast** (see p. 221).—The yeast cell is surrounded by a thin wall of cellulose and pectose. The living protoplasm enclosed within this wall secretes several enzymes, some of which are capable of diffusing through the



wall (and hence may be extracted by water or solvents), while others cannot do so, and can only be obtained by rupturing the cell walls and extracting. Such enzymes are called "intracellular" or "endo-enzymes," and obviously can only exert a chemical action on substances capable of diffusing through the cell wall into the living protoplasm.

The following enzymes occur in yeast (after Emil Schlichting) :—

**1. Hydrolysing Enzymes :—**

(a) **Sugar Splitting.**—Invertase, maltase, lactase, melibiase, raffinase, trehalase, diastase, and a glycogen-splitting yeast which plays an important part in self-fermentation or auto-digestion of the yeast cells. These enzymes have been treated on p. 221.

(b) **Proteolytic.**—Endotryptase. Plays an important part in auto-digestion of yeast cells. For properties, see p. 221.

(c) **Coagulating.**—Rennet, obtained by extracting yeast cells with  $\text{CHCl}_3$  under pressure at  $60^\circ \text{C}$ .

**2. Oxidising.**—Oxydase, catalase. Destroyed at  $60-65^\circ \text{C}$ .

**3. Reducing Enzymes.**—Optimum temperature,  $40^\circ \text{C}$ .

**4. Alcohol-producing Enzymes—Zymase.**—This directly splits up sugar into alcohol and  $\text{CO}_2$ , and is the cause of the alcoholic fermentation produced by yeast. Described p. 221.

**Chemical Composition of Yeast.**—The following analyses are typical of ash-free dry yeast substances (different samples vary) :—

	C	H	N
Top Yeast	48.6	6.8	11.5
Bottom Yeast	45.0	6.7	8.7

Old yeast is poorer in N. Moisture, 75-83 per cent. ; S, 0.39-0.7 per cent.

**Yeast Ash** varies from 2.5-11.5 per cent., and consists, approximately, of :—

$\text{KH}_2\text{PO}_4 + \text{K}_2\text{HPO}_4$	= 81.6	per cent. (top)	to 68	per cent. (bottom).
$\text{Mg}_3(\text{PO}_4)_2$	= 16.8	"	"	22.6 "
$\text{Ca}_3(\text{PO}_4)_2$	= 2.3	"	"	9.7 "

$\text{P}_2\text{O}_5$ , 54-59 per cent. ;  $\text{K}_2\text{O}$ , 28-40 per cent. ;  $\text{MgO}$ , 6-8 per cent. ;  $\text{CaO}$ , 1-4 per cent. Small amounts of chlorides, sulphates, etc.

**Structure and Life Conditions of Yeast.**—The ordinary beer yeast consists of minute egg-shaped single cells, about 0.01 mm. diameter. The cell consists of protoplasm enclosed by a cellulose cell wall and containing a spherical or disc-shaped nucleus, which can be made visible by staining. Vacuoles appear at the end of fermentation filled with a low-refractive fluid, also "granules" or "oil-drops" appear consisting of highly-refractive round or angular bodies. Besides vegetative propagation by budding, yeast also forms endospores under special conditions, the cell dividing into two to four spores which then germinate into new yeast cells. The spores of "culture" yeasts appear to be *empty*, while the spores of "wild" yeast are strongly refractive. Hansen has used the different spore formation to differentiate between the various types of culture and pure yeast.

Yeast is killed when heated in water to  $75^\circ \text{C}$ ., but when dry will stand a temperature of  $+100^\circ \text{C}$ . to  $-130^\circ \text{C}$ . Cooling for months is not detrimental to yeasts. Drying in a finely divided condition kills yeast after a few days. Yeast causes alcoholic fermentation between  $0^\circ \text{C}$ . and  $50^\circ \text{C}$ . The optimum temperature is  $28^\circ-34^\circ \text{C}$ . Yeasts retain their vitality longest in a 10 per cent. sucrose solution. Samples have been kept alive for over twenty years (Hansen) in this solution. A 22-25 per cent. sugar solution is completely fermented by most yeast races, but they refuse to grow in a 60 per cent. sugar solution. Yeasts require for their growth certain organic and inorganic salts, such as nitrogen compounds (amides, peptones), phosphates, sulphates, potassium, and magnesium salts—such are invariably found in grape juice and beer wort. Hence, although yeast will cause fermentation in a pure cane sugar solution, yet they cannot *grow* in this solution as the necessary



food stuffs are wanting. The presence of oxygen is also necessary in order to stimulate the first growth of yeast—hence the practice of blowing air through growing yeast.

Alcohol poisons yeast. In a solution containing only 5 per cent. by volume of alcohol, most yeasts cease to propagate. The enzymes in the yeast cell, however, are not much affected by this amount of alcohol, since some of the more powerful yeasts will generate a solution containing 18-19 per cent. alcohol, while wine yeasts have been known to ferment the solution until it contains 19 or 20 per cent. of alcohol. Nevertheless such yeasts cease to propagate in a solution containing more than 10-12 per cent. of alcohol. Distillery yeasts in concentrated mashes produce a solution containing usually 10-12 per cent. of alcohol. Fermentation is not likely to progress in a solution containing more than 20 per cent. by weight of fermentable matter.

Among yeast poisons are mercuric chloride, copper sulphate, phenol, formaldehyde, salicylic acid, hydrofluoric acid, sulphurous acid, carbon disulphide, chloroform, ether, and "antiseptics" generally (see p. 241). Free acids (especially the volatile fatty acids) and bases also exert a deleterious effect on yeast. Yeast, however, will bear the presence of a considerable quantity of lactic acid (see p. 235).

**The Chief Yeast Races.**—An enormous number of different races exist, each characterised by producing alcoholic liquors of different flavours and characteristics.\* We may divide them into two great classes:—

- (a) **Culture Yeasts**, e.g., *S. cerevisiæ*, *S. ellipsoideus*.
- (b) **Wild Yeasts**, e.g., *S. pastorianus*.

### (a) Culture Yeasts

Culture yeasts have been cultivated for long periods of time in the fermentation industries, and consequently have acquired characteristics which make them especially valuable for the production of alcoholic liquors.

We may classify culture yeasts thus:—

*Saccharomyces cerevisiæ*.—Top (high) yeast; bottom (low) yeast.  
 „ *ellipsoideus*.—Ferment of wine.

All these yeasts ferment the monosaccharides, also cane sugar and maltose, but not milk sugar.

Beer yeasts, distillery yeasts, compressed yeasts, and bakers' yeast all belong to the genus called *Saccharomyces cerevisiæ*, while yeasts for making wine belong to another genus, *Saccharomyces ellipsoideus*.

A yeast used for beer (brewery yeast) must generate certain substances possessing a characteristic aromatic taste or odour. It must also readily separate from the fluid, leaving a clear, bright liquid. A **distillery yeast**, on the other hand, must have a high fermenting power, in order to produce the maximum quantity of alcohol. A **baking yeast** should be rapid in action, and generate a large amount of alcohol and CO<sub>2</sub> in order to "raise" the dough. It should be noticed that a brewers' yeast is quite unsuited for use in a distillery, and *vice versa*.

**Beer Yeasts, Brewery Yeasts.**—These must clarify well, raise a good head, and generate a pleasant taste in the beer. Two well-marked varieties of these occur, namely, **top-fermentation** and **bottom-fermentation yeast**. They are sometimes called "high" and "low" yeasts respectively, the reference here being to the temperatures at which fermentation is carried on with them. The **high** or **top-fermentation** yeast is used to ferment infusion beers, and is the variety used by **English brewers**. They rise to the surface of the fermenting liquid, and grow best between 28°-34° C. The **low** or **bottom-fermentation** yeasts is the variety which brewers of lager beer (Germany and U.S.A.) employ in the fermentation of decoction worts. They settle at the bottom of the fermenting liquor and ferment at a low temperature of 4°-10° C.

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\* Many wild yeasts do not cause alcoholic fermentation at all.



When working with this low temperature, fermentation proceeds much less rapidly than with high yeast; growth and reproduction proceed more slowly, and the budding gives rise to less extensive colonies of cells; but the beer thus produced is usually richer in  $\text{CO}_2$  than that produced at a higher temperature.

The following are the chief brewery yeasts:—

**Top Yeasts.**—*Saccharomyces cerevisiae*, Hansen, from English and Scotch breweries, a vigorous beer top yeast. Yeasts for making **English Porter, Stout, Ale, Berliner Weissbiere, Lichtenhainer Beer, Braunbiere, Malzbiere.** The Institute for Gärungsgewerbe at Berlin breed two "top" yeasts, namely "Hefe A," a weak fermenting yeast, and "Hefe B," a powerful fermenting yeast.

**Bottom Yeasts.**—The following are the two chief types of German "bottom" yeasts: (1) Hefe "Frohberg"; (2) Hefe "Saaz." Between lie many intermediate varieties. Hansen (Copenhagen) cultivates **Carlsberg Bottom Yeast 1**, which produces a very stable beer, not readily clarifying, and **Carlsberg Bottom Yeast 2**, producing a beer not so stable as from 1, but clarifying more readily.

**Distillery Yeasts.**—These are top-fermentation yeasts. Distillery yeasts must cause a quiet but rapid fermentation, with formation of a high percentage of alcohol. They must be able to withstand a considerable amount of free acid, since the fermentation usually proceeds in fairly strongly soured solutions. It is not necessary that they should clarify well and raise a good head—in this they differ from brewery yeasts, where these are points of great importance.



Top-Fermenting Ale Yeast.

Bottom-Fermenting Lager Yeast.

FIG. 85.

The most important pure **distillery yeast** is **Race II., Berlin**, which was isolated in 1889 from a distillery in West Prussia. Suitable for fermenting highly concentrated mashes, possesses great power of resistance to high alcoholic content. For distilleries which ferment **molasses** and sugar refuse, characterised by a high percentage of various salts, the best yeasts to use are certain **wine yeasts**.

**Yeasts for Manufacturing "Compressed Yeast."**—"Compressed yeasts" are used by bakers for incorporating into dough. The  $\text{CO}_2$  gas generated by the fermentation, and also the alcoholic vapours when in the oven, puff up the bread and make it light. Bakers' yeast must have a pleasant taste and smell, develop rapidly and generate much  $\text{CO}_2$  and alcohol. It should also not be too sensitive to acid. **Berlin Race V.** is largely used for the manufacture of compressed yeast, also **Berlin Race XII.** is very suitable.

**Wine Yeasts.**—All belong to the species *Saccharomyces ellipsoideus*. These are found in very large quantities on ripe grapes, whence they get into the expressed grape juice or "must" and by fermenting the grape sugar present, convert it into wine.

An enormous number of distinct races occur, each one producing a wine of a different flavour. Each different wine district, in fact, possesses characteristic and distinct races of *Saccharomyces ellipsoideus*, and thus it comes about that wines from different districts, and even wine from the



same district but from different vineyards, can be readily distinguished by experts merely by their various tastes and bouquets.

Strictly speaking they are "wild" yeasts, since they occur free in nature, and have not, until quite recently, been systematically cultivated like brewery and distillery yeasts. Recently, however, pure cultures have been grown, capable of producing wine of definite specific characteristics. We prefer, therefore, to discuss their properties here as "culture" yeasts.

*Saccharomyces ellipsoideus*, T. Hansen, is a wine yeast, found by Hansen on the surface of ripe grapes in the Vosges district. The cells have an ellipsoidal shape. It is a bottom yeast, and ferments saccharose, dextrose, laevulose, and maltose, but not lactose. The different races of this variety not only produce wines of very different tastes and bouquets, but also exhibit very important differences as regards the amount of alcohol produced, and the way in which the fermentation proceeds. Some of these races actually manage to exist in a 60 per cent. sugar solution—a

property made use of in the production of "Melton Wine." In concentrated sugar solutions they produce much more alcohol than the species *Saccharomyces cerevisiae*. In some cases they produce liquids containing 20 per cent. of alcohol (see p. 244).

**Other Yeasts.** — *Saccharomyces pyriformis* (Marshall Ward) produces alcoholic fermentation of English ginger beer. Used in conjunction with the "ginger-beer" plant, *Bacterium vermiforme*. *Saccharomyces mali*, Du Clauxi, Kayser, from **cider**, ferments invert sugar and produces esters (bouquet).

*Schizosaccharomyces pombe*, the yeast in pombe (Negro millet beer), ferments dextrose; used in South American distilleries; *Schizosaccharomyces mellacei*, in Jamaica rum.

### (b) Wild Yeasts

The "wild" yeasts occur free in nature; they are not cultivated systematically like ordinary brewery or distillery yeasts, usually because they possess unpleasant characteristics and, indeed, often set up various "diseases" in beer, or affect the fermenting power of

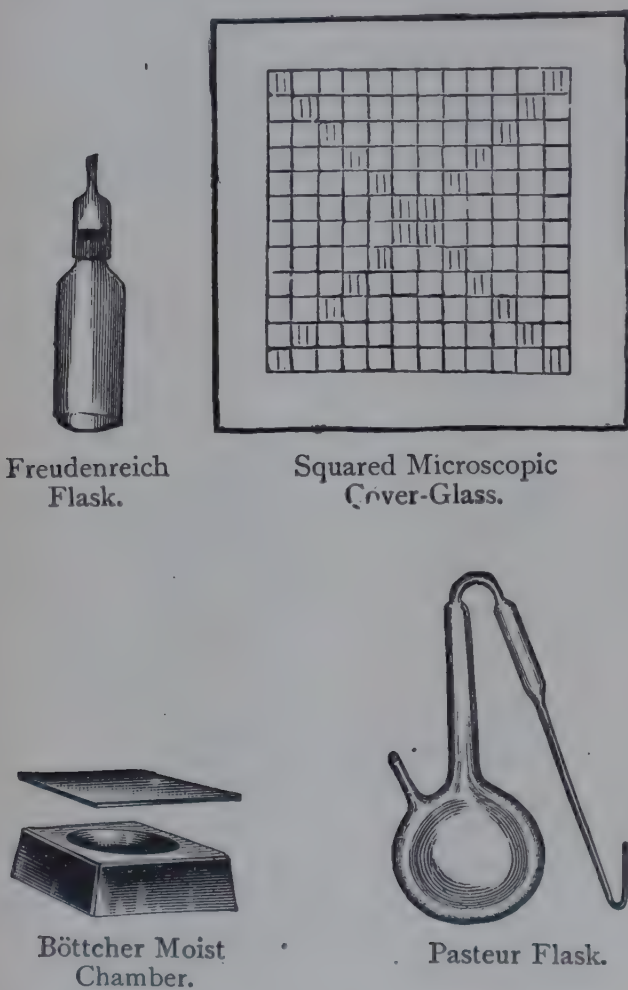


FIG. 86.—Apparatus for Pure Yeast Culture. Hansen's Method. (J. Griffin & Sons, London.)

infected yeasts. Thus *S. pastorianus I.* produces a bitter taste in beer, while *S. pastorianus III.* produces cloudiness. They occur as sausage-shaped cells. *Saccharomyces ellipsoideus II.*, Hansen, is a dangerous disease yeast for breweries, causing turbidity.

The "**Kahm**" yeasts (*Kahm Hefe*), e.g., *Mycoderma cerevisiae* and *vini*, consisting of round or elongated cells, form a skin on the surface of the fermenting liquor. They require oxygen; and can produce from sugar a small percentage of alcohol, but usually oxidise the alcohol directly to  $\text{CO}_2$  and water, with the rapid absorption of oxygen. *S. exiguus* (from compressed yeast) ferments monosaccharides and cane sugar, but not **maltose**. *S. apiculatus* also ferments only monosaccharides. Both are useless for the brewery. *S. ilicis* (bottom yeast) and *S. aquifolii*, Grönland, produce a bitter and disagreeable taste in worts.

*S. membranefaciens*, Hansen, found in wines and polluted waters. Generates **acids** from sugar. Propagates in presence of 12 per cent. alcohol. Destroys the bouquet of wines.

Certain **Moulds** also possess the power of fermenting sugar, e.g., *Mucor racemosus* (see under **Moulds**).



Hansen describes five varieties of wild yeast and gives their limits of size.

*S. cerevisiæ* var. *ellipsoideus* (4.5-9.5)  $\times$  (2.5-6.5)  $\mu$ .

*S.* „ „ *turbidans* (5-12)  $\times$  (2-9)  $\mu$ . Produces turbidity in beer.

*S. pastorianus* (3-17)  $\times$  (3-8)  $\mu$ . Impedes.

*S. intermedius* (4-16)  $\times$  (2-6.5)  $\mu$ . Does not appear harmful to beer.

*S. validus* (5-12)  $\times$  (1.5-5)  $\mu$ . Produces cloudiness in beer.

Will has isolated *S. willianus* (7.5-14)  $\times$  (3.5-6.5)  $\mu$  which produces a sweet, changing to bitter, taste of rotten fruit in beer.

*S. bayanos* (7-11)  $\times$  (5-6)  $\mu$  has also been isolated by Will.

*S. theomantitonum* Johnson possesses comparatively great resistance to heat and has technical applications in the tropics. It will ferment well at 104°-113° F., and will survive at 184° F. Stelling-Dekker classifies it with *S. cerevisiæ* var. *ellipsoideus*.

**Infection of Sugar Solutions.**—Ward and Baker gave the name *S. festinans* to a wild yeast which is particularly liable to develop in sugar solutions. It ferments extremely rapidly and produces a haze near the surface of primed beer. The dimensions of the yeast lie between (9-19)  $\times$  (5.5-4.5)  $\mu$ . It does not readily produce spores. Stelling-Dekker classifies it as *S. cerevisiæ* var. *festinans*.

A very good account of many other yeasts is given in H. Lloyd Hind's books on brewing (*q.v.*).

These other yeasts may be classified as asporogenous yeasts (*i.e.*, they do not form spores).

Pasteur used the name "torula" for those yeast-like fungi which did not form the typical mycelia and did not cause alcoholic fermentation. Hansen limits this group to non-spore forming varieties.

The torulæ are widespread on fruits and are even in water. They are thus often found in breweries. Many are harmless owing to their restrictive powers of fermentation, but some cause turbidity in weak beers. It is thought that some of these yeasts are essential for the production of special flavours in beers.

Moulds are also encountered in breweries where they develop in dark, warm, moist places. The moulds throw out a mycelium of long, thread-like tubes which spread over the surface of the beer. It is through these tubes that the nutriment for the growth of the mould is obtained. The majority of these growths, however, grow on damp wood, and do not grow actually in the beer on account of the paucity of oxygen therein. These moulds may not be harmful in themselves but are a sign that conditions are suitable for the growth of more serious infections of yeasts and bacteria.





## Pure Cultivation of Yeast

**Hansen's Method of Pure Yeast Culture from a Single Cell.**—The individual yeast cells in a drop of fresh yeast are separated by thoroughly mixing twice in succession with sterilised water contained in Freudenreich flasks (see Fig. 86). A drop of the mixture is then transferred to a Freudenreich flask containing liquefied wort gelatine, and thoroughly mixed. A drop of the wort gelatine mixture is then spread in a thin layer on a squared microscopic cover-glass, left until set under a bell jar, then placed, gelatine film downward, over small moist chambers, called Böttcher chambers, containing a drop of water at the bottom of the cell. The slide is examined under the microscope and the positions of a number of individual yeast cells, which are several millimetres apart from other cells, are carefully marked. The culture is then kept in an incubator at 20° C. (68° F.). Each cell develops into a colony of cells. When the colonies are large enough a pure culture in sterilised wort is obtained by inoculating from each separate colony nutrient sterilised wort contained in a Pasteur's flask. In this way an absolutely pure culture is obtained from a single cell; these separate cultures are then examined as to their action on wort and the most suitable species selected for use in practice. The culture yeast is then transferred to larger quantities of a nutrient wort. The production of large quantities of pure cultivated yeast is accomplished in special pure culture apparatus (see below).

**Lindner's Method of Drop Culture** is a slight modification of Hansen's. He dips a pen into the diluted yeast, and draws a line with this on the under side of a sterilised microscopic slide, which is then fastened by means of vaseline on the hollow moist chamber for observation under the microscope. As the individual cells develop they are used to inoculate larger quantities of sterilised wort contained in Pasteur's flasks, as in Hansen's method. The method is easier than Hansen's, and the yeast cells can be more easily recognised.



FIG. 87.—Lindner's Method of Drop Culture.

## Apparatus for the Industrial Production of Pure Culture Yeast

**Hansen's Apparatus.**—The apparatus consists of three parts, viz.: (1) The air-pump A with the air reservoir B. (2) The wort cylinder D. (3) The fermentation cylinder C (see Fig. 88).

By means of the pump A air under a pressure of 3-4 atmospheres is forced into the air reservoir B, which is provided with a manometer and a safety-valve. The wort cylinder D is now sterilised with high-tension steam from the brewery boiler, which drives out all contained air through the pipe *n*, the end of which is covered by water in *o*. Next, the compressed air from B is allowed to rush into D, passing on its way through the cotton-wool filter *m*, which removes all germs. Boiling wort is now run into D through the pipe *u*. The wort is cooled to the proper temperature by means of a pipe *pp*, which sprays cold water over the surface of D. The proper amount of sterilised air for aeration is introduced through the cotton filter *m*. The fermentation cylinder C is now sterilised in exactly the same manner as D by means of tension steam. C is also supplied with sterilised air through the cotton-wool filter *g*, while a glass tube *ff*, connected with the cylinder by the pipes *e* and *h*, allows the level of the wort in C to be readily ascertained. A small pipe *j* and an indiarubber tube allows a small amount of pure yeast culture from a Pasteur flask to be introduced when required into the sterilised wort in C. The introduction of yeast need only be made once, when it develops in the wort and gives a continual supply of yeast for a year or more. The outlet tap *l* is arranged so that no infection from without can enter the interior of C. To ensure against this danger a considerable pressure of air in C is always present. The tube *kk* places the cylinders C and D in communication; and allows the transfer



of sterilised wort from D to C as required. When the level of liquid in C (as seen by the glass tube *ff*) nearly reaches J, the tap *k* is turned off, the yeast culture added through J, J is shut, *k* opened again, and the addition of wort from D continued until C is nearly filled (up to a mark on the glass tube), and the mass well stirred by the rousers *bbb*. In this way about 220 litres of wort is placed

under fermentation, with an absolutely pure yeast culture. After about ten days the beer formed is drawn off through the outlet tap *l*, compressed air being simultaneously allowed to enter through the filter *g*.

This operation is carried out as follows: First of all some of the dregs are allowed to run out through *l*, then *l* is closed, wort added until C is again filled to the mark (as seen in the glass tube *ff*), stirred, and then 27 l. of beer and yeast are run off through *l*. More wort is added, stirred up, and another 27 l. run off. The volumes run off are indicated by marks on the glass tube *ff*. The 54 l. of yeast liquid so obtained contain enough yeast to ferment 8 hectolitres of wort. The rest of the yeast, still contained in C, is allowed to ferment another

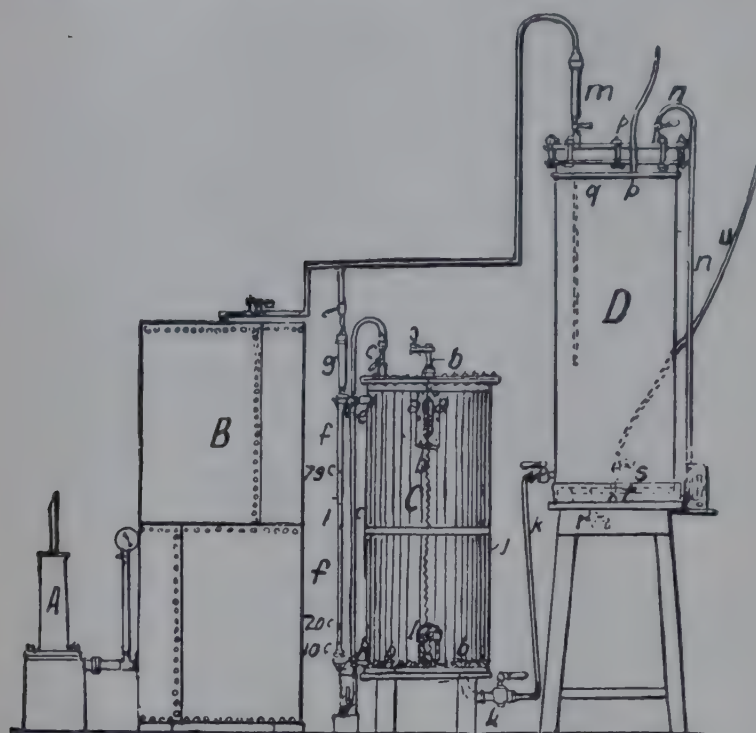


FIG. 88.—Hansen's Apparatus for Pure Yeast Culture.  
(By permission of The Review Press Ltd. From  
Jørgensen's "Pure Yeast Management.")

220 l. of wort from C, and can be again drawn off as before. In this way a continuous supply of pure yeast culture can be obtained from C.

**Lindner's Small Pure Yeast Culture Apparatus.**—This is capable of producing 1 kg. yeast. The apparatus consists of a cylinder A and a flask B, which is connected up through the safety bottle C with an ordinary filter pump D. 50-60 l.

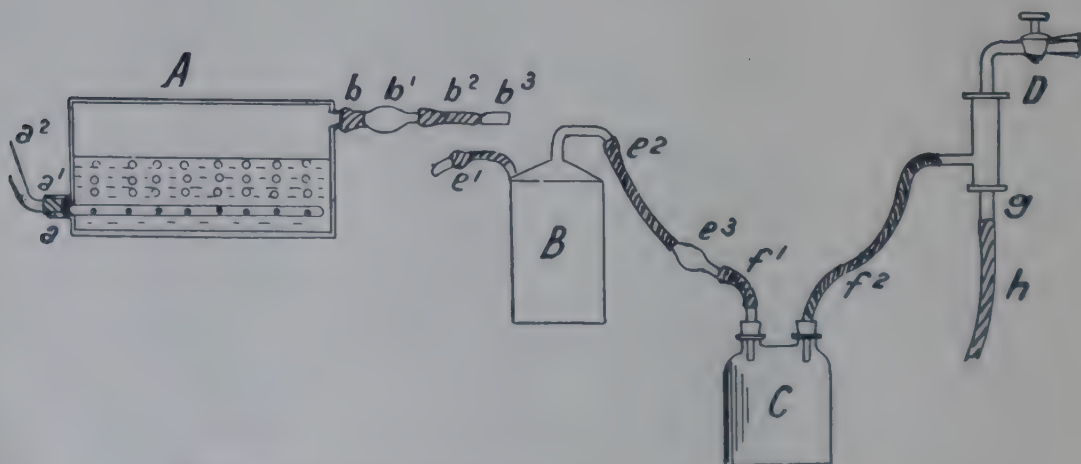


FIG. 89.—Lindner's Small Pure Yeast Culture Apparatus.

of wort are sterilised in A and caused to ferment by a pure yeast culture contained in B, while air is sucked through the apparatus by means of D, A and B being joined up together for the purpose. The incoming air is sterilised by passing through a sterilised (at 150°-160° C. in air oven for two hours) cotton-wool filter attached at *a*<sup>2</sup>. *e*<sup>3</sup> is another such cotton-wool filter to prevent infection reaching B.



**Lindner's Large Pure Yeast Culture Plant.**—This consists of the large sterilising and fermentating copper cylinder A and the culture yeast flask B (or C). A number of tubes lead into A, by means of which steam, water, wort, or air can be introduced. The contents can be agitated by means of a sterilised air blast which is passed in through the coil *d*. The wort in A is sterilised by tension steam, cooled, impregnated with pure culture yeast from B, and, when sufficient yeast has grown in A, the contents are emptied through *i* and *e*, leaving, however, sufficient fluid in the apparatus to fill B, so as to have a supply of the same kind of yeast so as to start the operation over again when A is again refilled with sterilised wort.

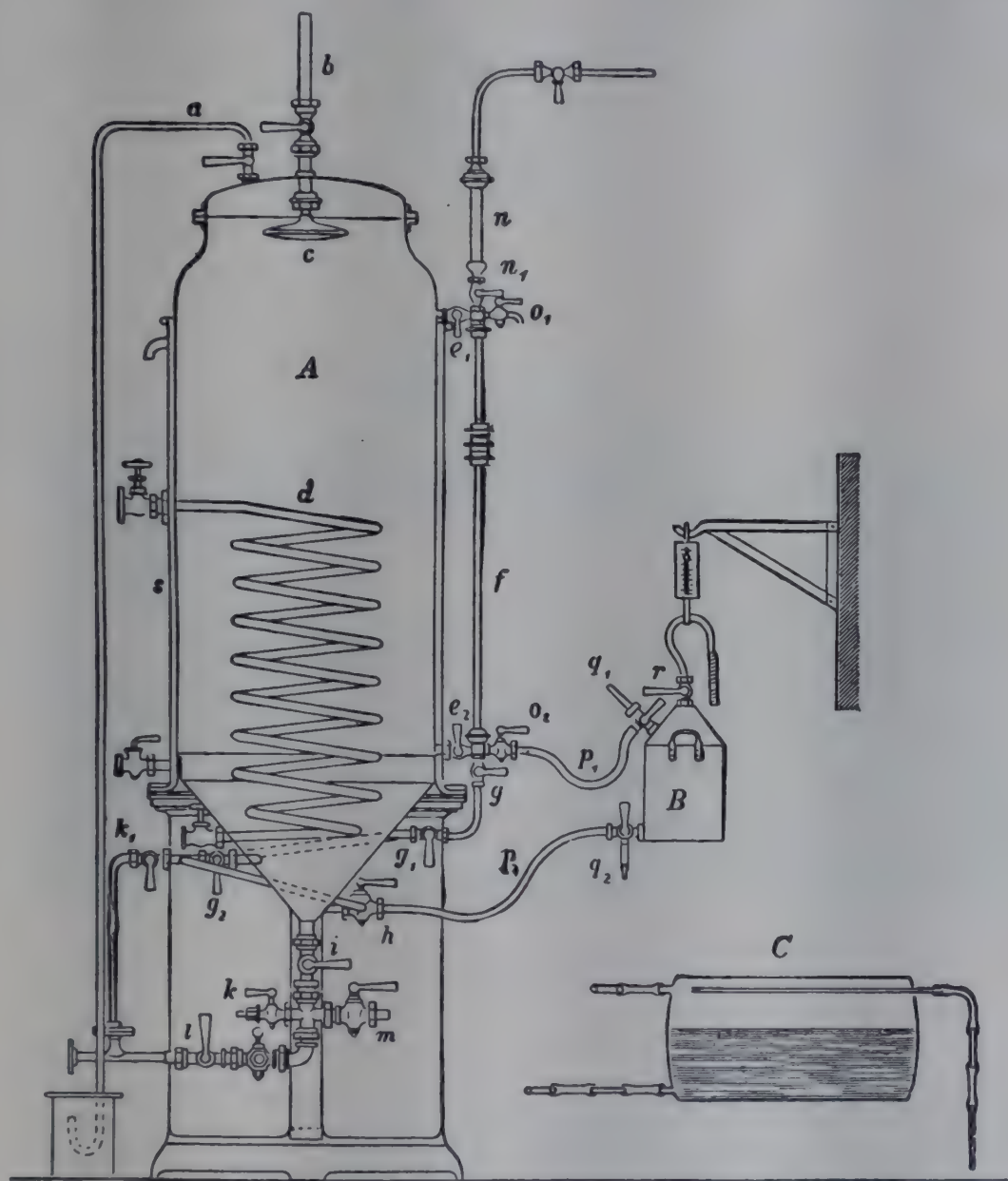


FIG. 90.—Lindner's Large Pure Yeast Culture Plant.  
(Manufactured by F. W. Pest, Berlin.)

*Hansen* was the first to introduce the production and application of pure culture yeast in **bottom-fermenting** breweries, and his methods have abolished all empiricism and replaced it by absolutely safe working methods in practice.

*Jørgensen* since 1885 has applied the pure culture of **top-fermenting** yeast, but the success in practice has not been so marked as with the **bottom-fermenting** varieties (see under **Beer**).

It should be noticed that pure culture alcohol yeast is not only free from all disease-producing germs, but consists of *one single species only*. It is used as a "pitching" yeast in the brewery. As soon as the biological tests and control show any deterioration of the pitching yeast, it is discarded and is replaced by the new pure culture yeast, which is kept continually growing in the pure culture apparatus. The pitching yeast is thus periodically replaced by pure culture yeast. Nevertheless, in the course of time the pure culture yeast itself may begin to degenerate, owing to its progressive alteration into species of yeast exhibiting undesirable properties, the fermenting liquor developing



a flavour different to the normal one in this case. When this occurs it will be found that *not all the cells degenerate simultaneously*—some are unchanged. Consequently a sample of the yeast is taken and a dilution made, the individual cells being well separated from one another, and a comparative series of fermentations made with the different individual cells show that there are differences between these cells. Some of the new growths will show the newly developed disagreeable characters, but others will be found to be cells which have not changed their character. Pure single cell cultures are then made from the unchanged varieties, as previously described, and a culture obtained similar to the original.

### Manufacture of Compressed Yeast

Bakers use yeast extensively for mixing with the dough. It generates  $\text{CO}_2$  and alcohol from the dextrose and maltose formed in the bread during the raising and kneading process. In baking, the alcohol assists the  $\text{CO}_2$  in causing sponginess of bread owing to its vaporisation\* during the heating. Bottom-fermenting yeast is too slow in action and bitter for this purpose, while ordinary brewery yeasts (top) are also not suitable on account of their "hop" flavour. The species now used is a distillery top yeast, and, being sold in a compressed state, is known as "compressed yeast."

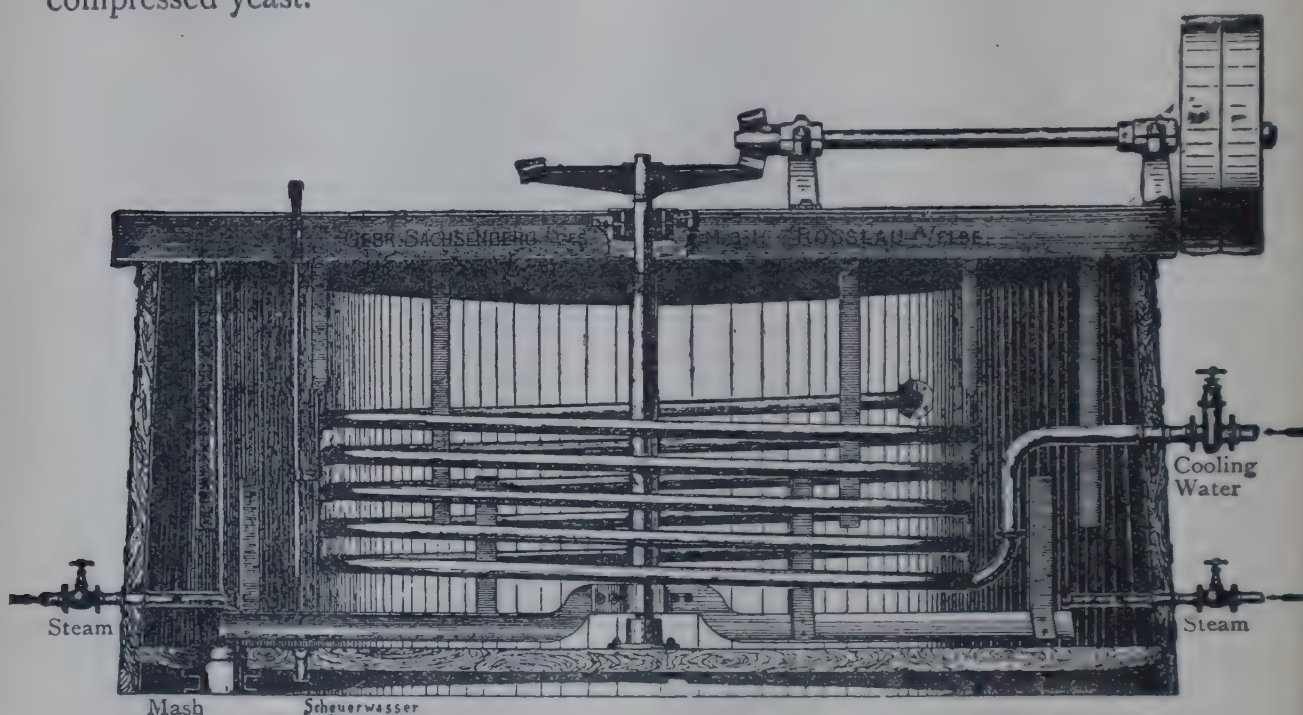


FIG. 91.—Horizontal Mash and Acidifying Apparatus for Compressed Yeast Manufacture.  
(Gebrüder Sachsenberg, Rosslau in Anhalt, Germany.)

Compressed yeast manufactories are always grain distilleries, and, indeed, are the largest of this kind. Thus one of the largest compressed yeast manufactories in the world, Helbing of Hamburg, produces yearly 2,500 tons of compressed yeast, 25,000 hl.† of alcohol (100 per cent.) in the form of spirits, etc., and, daily, 2,000 hl. of spent wash, which is partly used fresh as a cattle food, and partly sold in a dry state. The Fleischmann Manufacturing Company, U.S.A., is another enormous concern of the same kind. To show the magnitude of the industry we may mention that in 1904-5 Germany alone produced 36,730 tons of compressed yeast (1,350 tons being exported to England) and 482,000 hl. alcohol (100 per cent.).

\* **Baking Powder** is used as a substitute for yeast, a chemical generation of  $\text{CO}_2$  gas causing the dough to rise.

A common baking has the composition: 34 sodium bicarbonate + 25 cream of tartar + 40 starch. Use 15-20 parts to 500 parts flour. For cakes use 1 sodium bicarbonate + 2 cream of tartar + 15 flour, or 10 sodium bicarbonate + 7.5 tartaric acid + 17 starch. In bread making sometimes dilute HCl (or calcium biphosphate) is mixed into the dough and then sodium bicarbonate is stirred in.

A common "self-raising" flour is: 10,000 wheat flour + 190 cream of tartar + 85 sodium bicarbonate.

† 1 hl. = 1,000 litres = 220.1 gallons.



Compressed yeast is produced by two different methods, viz., the "old" method, such as is used in ordinary distilleries, and the modern and more economical "aeration method."

**Old Method for Producing Compressed Yeast.**—A mixture of malt and 1.5 parts rye or wheat are mashed (see under **Spirits**) at a convenient temperature, so as to obtain as complete a transformation as possible of the starch into maltose. The mash is allowed to stand in the vat (Fig. 91) at about  $35^{\circ}\text{C}$ ., the temperature most suitable for the production of lactic acid. The lactic acid bacteria rapidly multiply—in modern practice pure lactic acid bacteria are sometimes added—and a marked acidulation develops. The lactic acid organism is peculiarly sensitive to its own product, and ceases to develop after 1.5 per cent. of lactic acid has been formed. The presence of lactic acid prevents the undue development of bacteria and wild yeasts, also it peptonises the nitrogenous matters of the grains in the mash so as to render them available as yeast foods. Sufficient acidulation being produced the mash is cooled to  $25^{\circ}\text{C}$ ., yeast is added, and fermentation allowed to proceed for ten to eighteen hours.

When the yeast is "ripe"—i.e., when it has ceased to grow, and so is free from small daughter cells—and when most of the yeast has been forced to the surface of the liquid by the  $\text{CO}_2$ , the yeast is skimmed off from the surface of the liquid, filtered through fine gauze in order to free it from malt husks, etc., washed with cold water, and pressed in *filter presses*. The mash remaining is allowed to ferment with the yeast still left in the liquid for about twenty-four hours longer, and then is distilled for alcohol.

**New Aeration Method of Manufacturing Compressed Yeast.**—This process makes use of the fact that yeast requires oxygen for its full development; it differs from the previous method in that clear filtered worts are used for fermentation so that practically all the yeast formed is isolated.

The mash contains more maize and less rye than in the old process, and contains a considerable amount of the nitrogen-rich malt germ and green malt. The mash is allowed to sour (as before) with lactic acid, up to 0.6 per cent., at  $50^{\circ}\text{C}$ ., is sterilised at  $65^{\circ}\text{C}$ ., filtered, cooled to  $30^{\circ}\text{C}$ ., and pitched with yeast. The fermentation takes place in vats (Fig. 92) through which a continual and powerful stream of air is forced from perforated tubes at the bottom of the vat, while the temperature is maintained at  $30^{\circ}\text{C}$  by a heating coil. After twenty-eight hours or so the sugar is all fermented, and the yeast ceases to grow, i.e., becomes "ripe" and free from budding cells. The yeast is then separated from the clear fermented liquor, by passing through centrifugal machines (Fig. 93) (Laval separators), similar to those

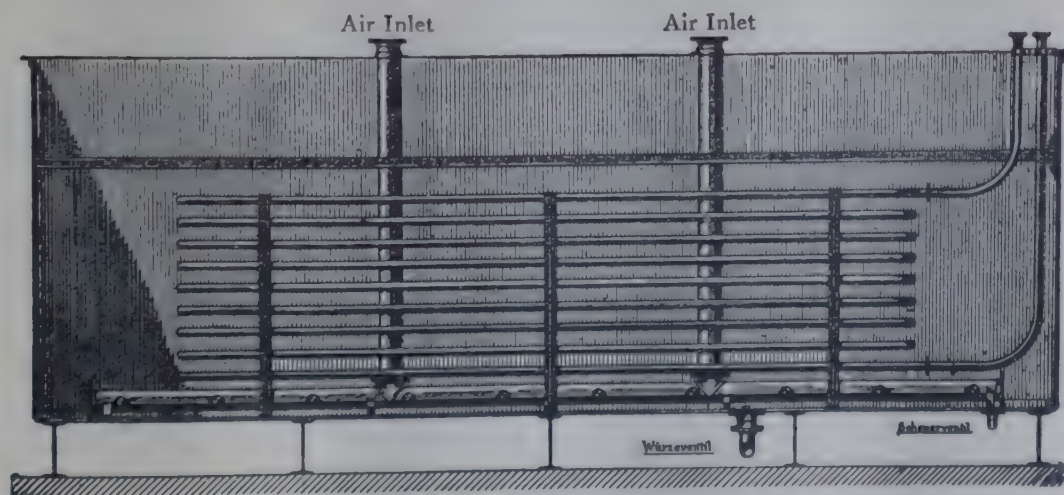


FIG. 92.—Modern Iron Fermenting Vat, showing best distribution of air for Aerated Yeast Manufacture.

(Gebrüder Sachsenberg, Rossau in Anhalt, Germany.)



used for separating cream from milk, and is then pressed dry in filter presses, sometimes with the addition of starch. The clear residual mash is then distilled for alcohol (see **Spirit Distillation**).

By this process 100 kg. of grain yield 23 kg. of good compressed yeast containing 70 per cent. water and 18 l. of 100 per cent. alcohol. Under favourable conditions over 30 kg. yeast and 15 l. alcohol are obtainable. The old process only produced 14 kg. yeast but more alcohol, viz., 28 l.

Although the presence of air favours the development of wild yeasts and bacteria, the initial souring of the mash prevents their development to any serious

extent, and "aerated" yeast is now quite as energetic a raising agent as the best yeast as manufactured by the older process. Nevertheless the mother yeast, from which the crop is raised, is usually bred by the older process.

Formerly it was the custom to add to the yeast a certain amount of starch before pressing, as a drier product with better keeping powers was thus obtained. The modern yeast races used, however, are now so improved that they are no longer "slimy," and are easily pressed dry; consequently starch is now no longer necessary. If added (especially if for lowering the price of the product) its presence and amount should be stated on the label.

Compressed yeast will keep a long time when securely packed (best in tinfoil) and kept at 8°-12° C. But when exposed to air or in warm weather it rapidly becomes stale and deteriorates. Completely dried yeast will keep for years, but is lacking in fermentative power. The ultimate aim of the yeast manufacturers, namely, the propagation and growing of the yeast without

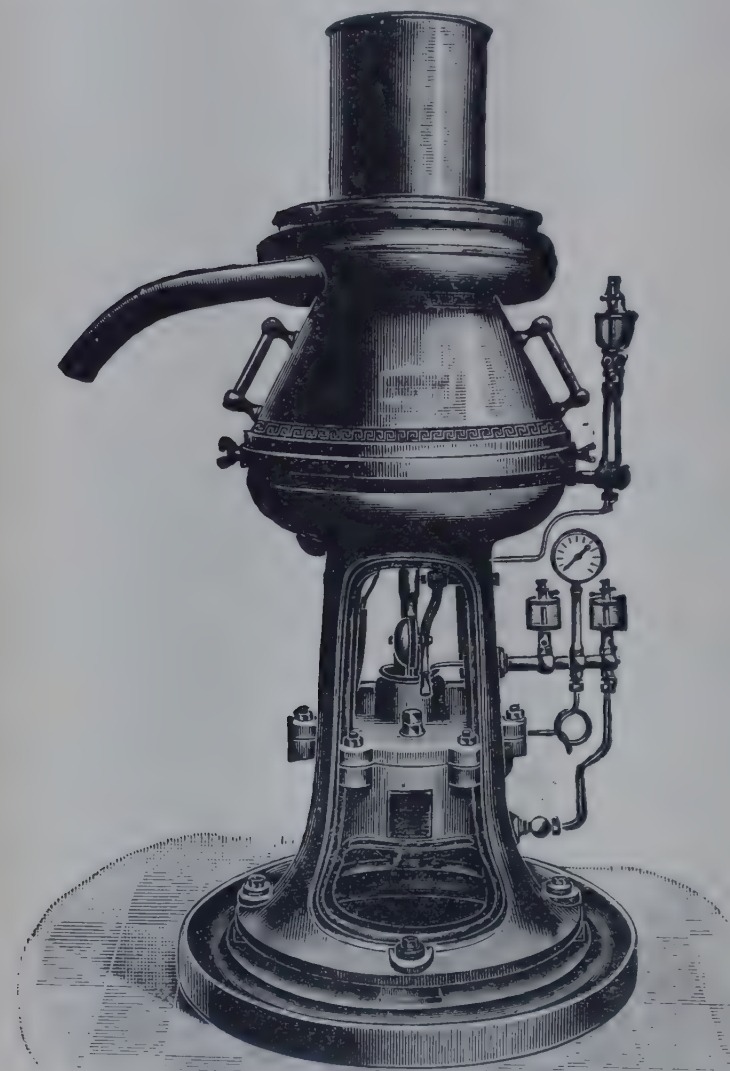


FIG. 93.—Yeast Centrifugal Separator with Steam Turbine.  
(Made by Gebrüder Sachsenberg, Rossau in  
Anhalt, Germany.)

the simultaneous production of spirits, has not yet been achieved, although it is, perhaps, a theoretical possibility.

**Statistics.**—In 1910 England imported 203,900 cwt. of yeast of value £394,121. Of this quantity the Netherlands supplied 106,500 cwt., Belgium 48,500 cwt., France 26,000 cwt., Germany 18,600 cwt. The United States in 1910 exported \$71,000 of yeast, Canada taking \$55,000. Germany produces annually about 800,000 cwt. of yeast.

For modern statistics see Appendix III.

### Chemical Analysis of Yeast

The yeast, which should have a pleasant aromatic smell, is first examined under the microscope (600-800 power), and the form, shape, and size of the cells observed. Old yeast differs in appearance from young yeast. The number of dead cells present are ascertained by adding to the solution



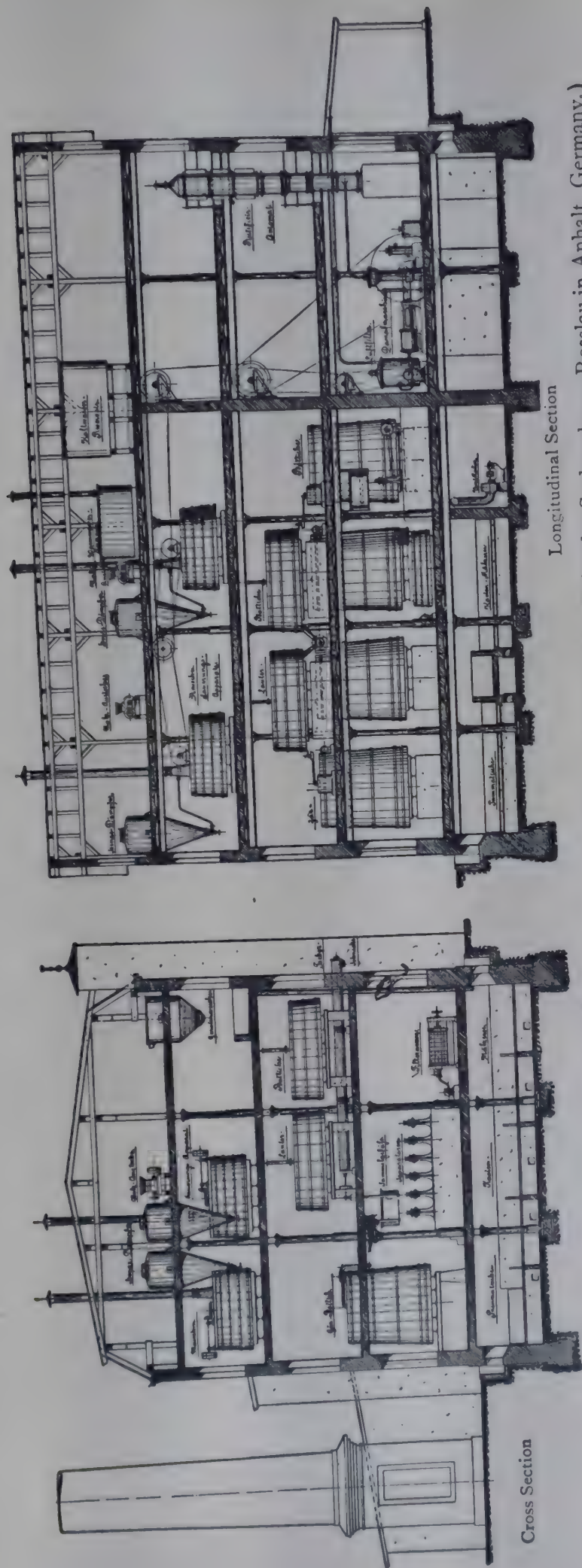


FIG. 94.—Sections through a Compressed Yeast Factory, Aeration Method. (Designed by Gebrüder Sachsenberg, Rosslau in Anhalt, Germany.)

a drop of methyl violet, eosin, or fuchsine in alcohol. Dead cells stain, but living ones are unaffected. The presence of bacteria, etc., may be detected by their different shapes. Next, the detection of wild yeasts is carried out by using Hansen's method of **spore culture** on blocks of sterilised gypsum (see Jørgensen's "Practical Yeast," p. 9).

The difference between the spores of "culture" yeasts and "wild" yeasts is so great that one quickly notices it on placing the slide under the microscope. The water and ash of a yeast are determined according to the standard methods of food analysis.

The **fermenting power** of a yeast, *i.e.*, the rapidity with which it decomposes sugar, turning it into  $\text{CO}_2$  and alcohol—is especially required for the valuation of compressed yeast. **Meissl's Method** determines the *weight* of  $\text{CO}_2$  which is generated by 1 g. of yeast within six hours at  $30^\circ \text{C}$ . from a solution in ordinary tap water of 400 g. pure sucrose, 25 g. ammonium phosphate, and 25 g. potassium phosphate. A yeast generating in this time 1.75 g.  $\text{CO}_2$  is stated to have a *fermentative power* = 100 and be a "normal one."

**Hayduck** and **Kusserow's** methods measure the *volume* of  $\text{CO}_2$  generated by a given quantity of yeast in a certain sugar solution. For details see the special works referred to above; also Dr Slator's article below.

The amount of starch present—which may vary from 5-50 per cent.—is estimated in the usual way.

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## II.—THE RATE OF ALCOHOLIC FERMENTATION BY LIVING YEAST

BY ARTHUR SLATER, D.Sc., Ph.D.

With slight additions by E. I. COOKE, M.A.(Cantab.), B.Sc., A.R.I.C.

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H. LLOYD HIND.—“Brewing, Science and Practice,” vol. ii., p. 783. Chapman & Hall.

The rate of fermentation by living yeast depends on certain factors which have been fairly accurately determined. An excellent account of the matter is given in Dr A. Harden's monograph on “Alcoholic Fermentation” (London, 1911) to which the reader is referred for further particulars.

A convenient apparatus for measuring such rates is shown in the accompanying figure.

A glass bottle of about 150 c.c. capacity is fitted with a rubber bung and connected by pressure tubing to a mercury manometer which can register pressures from a vacuum to about 30 cm. of mercury. The apparatus can be exhausted and kept air-tight by means of a side piece and a stopcock.

The fermenting solution is introduced into the bottle, and the apparatus is then exhausted. The bottle, which rests in a thermostat, is shaken at definite intervals of time, and the amount of fermentation is measured by the change in pressure. To assist in the shaking twenty glass beads of about the size of peas are placed in the bottle. The apparatus can be calibrated by fermenting completely 0.1 g. dextrose in the bottle and observing the corresponding change in pressure.

**The Rate of Fermentation of Dextrose.**—The factors which influence this rate have been determined by making up definite solutions of dextrose and adding yeast in known amounts. The liquid is transferred to the bottle of the apparatus and the initial rate of fermentation measured in the manner described.

The rate of fermentation of dextrose is almost independent of the concentration of the sugar if the solution is not too concentrated or too dilute.

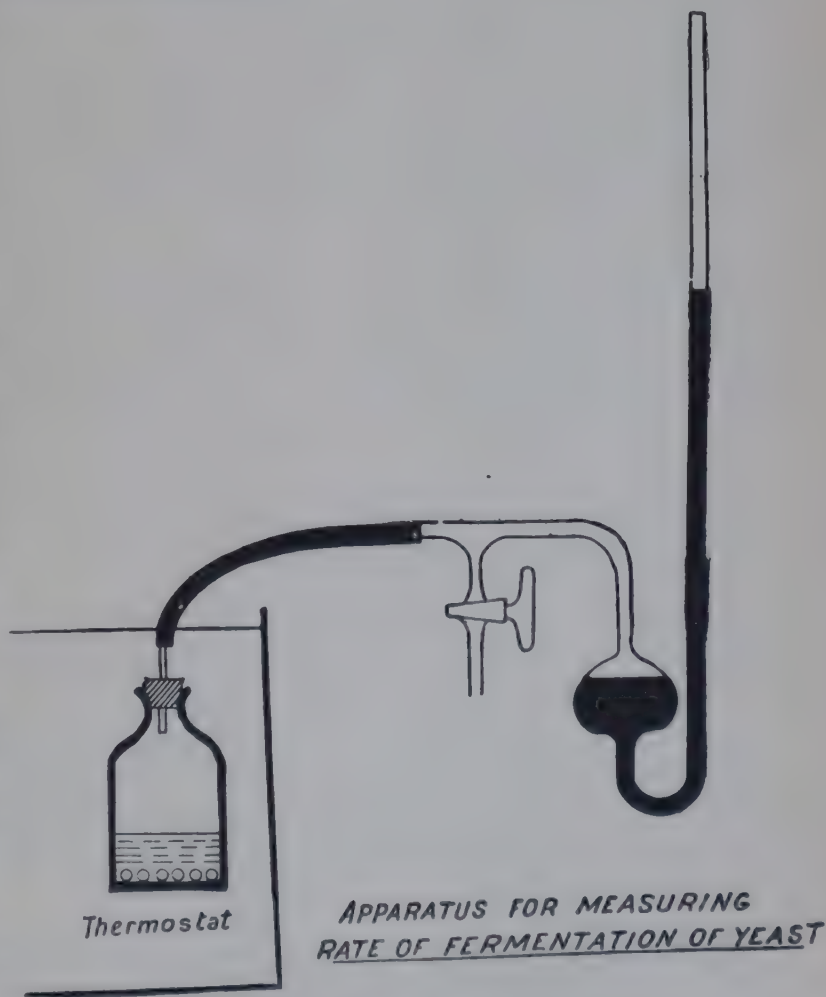


FIG. 95.

The rate of fermentation is exactly proportional to the amount of yeast present.

It can be shown that the diffusion of the sugar into the yeast cell takes place so rapidly that the yeast cell is efficiently supplied with sugar even at very dilute concentrations.

The influence of temperature on the rate of fermentation is very great. The activity of a yeast cell is almost entirely dependent on the temperature, and it is possible to construct a table showing the activity of a yeast cell at various temperatures.

The following table refers to a brewery yeast. The activity column gives the number of grams per second fermented by  $10^{14}$  yeast cells.

Temperature. C.	Activity.	Temperature. C.	Activity.
40	5.05	20	1.30
35	4.05	15	0.68
30	3.00	10	0.345
25	2.08	5	0.14

### The Rate of Fermentation of Different Sugars

**Laevulose** is fermented by various yeasts at the same rate as dextrose.

**Mannose** is probably fermented by all yeasts which ferment dextrose, but the two rates differ—in some cases dextrose is fermented more rapidly than mannose, in other cases the reverse happens.

Fresh samples of yeast ferment mannose more rapidly than dextrose, but by older samples the glucose is more rapidly decomposed.

**Galactose.**—Only certain species of yeast are capable of fermenting this sugar, even though they ferment dextrose, laevulose, and mannose readily. The special interest in the fermentation of this sugar consists in the fact that even these special yeasts cannot ferment the sugar unless they have previously been acclimatised by growth in the presence of galactose.

**Sucrose (cane sugar)** can only be fermented by yeasts which contain the enzyme "Invertase," which converts the sugar into dextrose and laevulose (invert sugar). Most culture yeasts contain this enzyme and are capable of fermenting sucrose as rapidly as dextrose. The invert sugar is produced more rapidly than it is fermented, and so accumulates in the fermenting solution.

**Maltose** is fermented by yeasts which contain the enzyme "Maltase." This enzyme is also present in most yeasts used technically, and such yeasts ferment maltose almost as rapidly as dextrose.

**Lactose.**—A few varieties of yeasts contain the enzyme "Lactase" and ferment lactose (milk sugar).

**Glycogen.**—The autofermentation of yeast consists in the transformation of the glycogen in the yeast cell to alcohol and carbon dioxide. The rate of the autofermentation depends on the amount of glycogen in the yeast cell, which varies according to the age of the yeast. With fresh yeast the rate is about one-tenth the rate of the fermentation of dextrose, with older samples the rate may fall to one-fortieth of the value.

**Malt Wort.**—The rate of fermentation of malt wort (p. 273) during the first part of the fermentation is the same as that of dextrose. The temperature and the number of yeast cells are therefore the main factors which determine this rate.

Malt wort contains the necessary food for yeast growth, and the amount of yeast increases for some time after seeding. The number of yeast cells depends, therefore, on the seeding and the growth which has taken place. Yeast growth



does not continue indefinitely but attains a maximum which was found by A. J. Brown to be approximately independent of the amount of the seeding.

In all probability it is the changes in the medium caused by the yeast which determines this maximum growth. Thus the sugars which are necessary to yeast growth are transformed to alcohol and carbon dioxide, both of which inhibit yeast growth, and when this transformation is partly completed the yeast growth stops. This explanation also makes it easy to understand how different seedings have little influence on the final crop. If we consider two worts seeded with yeast one ten times the amount of the other, then if these concentrations are small compared with the final yeast crop the growth in the first case from one to ten is accompanied by hardly any change in the medium. The two would then be almost identical and produce the same final yeast crop. See also H. Lloyd Hind, "Brewing, Science and Practice." Chapman & Hall.

**The Retarding Influences of Antiseptics.**—Many substances, such as mercuric chloride, copper sulphate, phenol, salicylic acid, and many others, on addition to a fermenting solution, inhibit the reaction. These substances on addition in very dilute concentration are said to accelerate the reaction. It can be shown, however, that this acceleration is on the growth of yeast and not on the fermentation.

Phosphates which have such a remarkable accelerating influence on fermentation by yeast juice have no such influence on fermentation by living yeast (see p. 222).

**Intermediate Compounds in Fermentation.**—Chemists have long held the opinion that dextrose is first converted into some intermediate compound before the formation of alcohol and carbon dioxide. A compound of the formula  $C_3H_6O_3$  has been suggested, and the fermentation equation then reads—



Lactic acid and dihydroxyacetone both have this formula and both have been suggested as possible intermediate compounds. The lactic acid theory has been abandoned owing to general recognition that it is not fermentable. The slow rate of action of yeast on dihydroxyacetone makes the second suggestion also improbable.

See also Fernbach on "The Mechanism of Alcoholic Fermentation," *Jour. Inst. Brewing*, 1916, xxii., p. 354. See also *Compt. Rend.*, 1913, 157, 1478; 1914, 158, 1719, where the question of the presence of pyruvic acid is dealt with.

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### III.—WINE

By G. MARTIN, Ph.D., D.Sc.

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- G. JACQUEMIN.—*Jour. Inst. Brewing*, 1899, v., 321; *Compt. Rend.*, 1899, 128, 369.

WINE is an alcoholic fluid prepared without distillation by the fermentation of grape juice. The fermentation takes place spontaneously under the influence of special wine yeasts (*Saccharomyces ellipsoideus*) which occur naturally on grape skins and in the air.

The vine, *Vitis vinifera*, grows freely in Europe, Asia, and America. It requires an average temperature of 10°-11° C., and an average summer temperature of 18°-20° C.; while ripening it requires much sunshine in order that sugar may be formed. A climate with hot summers and severe winters is often very favourable for the cultivation of the vine. During the growth, rain is necessary, but when ripening only bright sunshine should reach the fruit. The weather has a very great influence on the growth of the vine. The soil is not so important, but warm loose soil—especially volcanic soil—is best. The soils must be rich in potash. The best vines are grown along the banks of the Rhine, in Southern Italy, in the Greek Islands, Spain, Austria, Southern France, Australia, Asia Minor, etc. France produces the largest quantity of wine, producing on an average 45,000,000 hl. annually, in value over 1,000,000,000 francs. Then follow, in order, Italy, Spain, Austria-Hungary, and Germany. In Asia Minor the vine is very extensively cultivated, but is utilised principally for the production of raisins (dried grapes).

It should be noticed that grapes are used not only for the production of wine, but also for the manufacture of raisins (dried grapes); in the manufacture of genuine grape sugar, of cognac brandy, wine-vinegar, etc. From wine lees are obtained tartar and tartaric acid; an oil is obtained from the seeds.

The riper the grape the more sugar it contains, and the richer in alcohol the resultant wine; consequently the grapes are never gathered until perfectly ripe, when it then contains, usually, 15-20 per cent. of sugar, and in exceptional cases 10-30 per cent. sugar. The sugar is a mixture of dextrose and laevulose, no sucrose (cane sugar) being present. The amount of free acid in the juice varies from 2.9 per cent. (unripe) to 0.9 per cent. (ripe), the acids being tartaric and a small amount of malic.

**Pressing the Grapes.**—The hard and sour grapes begin to become soft and sweet towards the end of August; at the end of October or beginning of November the sugar is at a maximum, and the grapes are plucked and pressed.

This latter operation is carried out by placing them in a wooden tub and stamping with a wooden maul or pestle to extract the juice. Sometimes they undergo instead a preliminary crushing by foot, other times they are ground in grape mills with wooden rollers.



If **White Wine** is required the juice is rapidly pressed away from the grape skins, stalks, etc., in special wooden presses. The best presses are the screw presses made of wood or cast iron. The clear juice runs through holes in the floor into the wooden fermenting vats.

If **Red Wine** is required, the stalks are carefully separated from the grapes, which are then macerated, and the mass allowed to ferment. When this occurs the alcohol generated extracts the red colouring matter from the fermenting grape skins, and the liquid acquires the fine red colour characteristic of red wine. Simultaneously a considerable amount of tannic acid enters the fluid.

It should be particularly noticed that *purple* or *red* grapes if pressed away from skins *before* fermentation yield a **white wine**. The red colour is only obtained when the skins are left in contact with the fermenting liquid for a suitable time—several days—and the liquid is then pressed away from the residual grape skins.

100 parts of grapes yield 60-90 parts of **must**, as the grape juice is called. The richest grapes are the first to yield juice when placed in the press. The juice

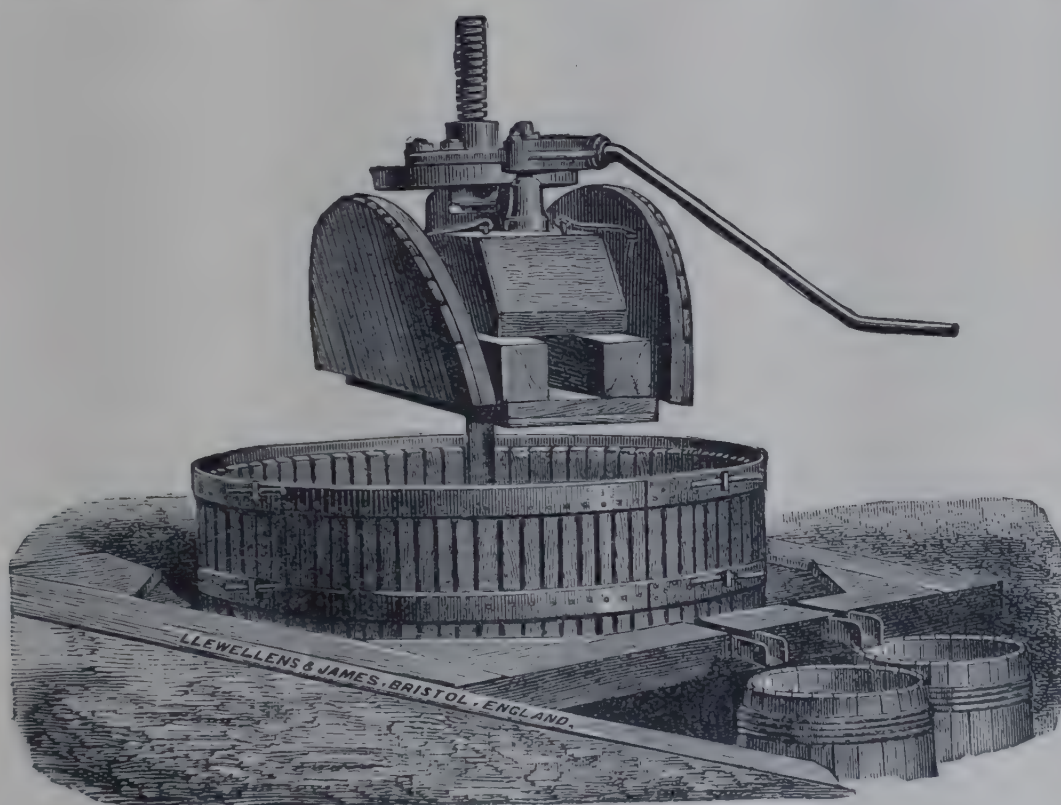


FIG. 96.—Wine Press. (Llewellyns & James, Bristol.)

obtained from the first pressing produces the best wine—the so-called “first wine.” The second pressing, using greater pressures, yields a **must** containing more acid, and from this is obtained the “press-wines.” The third pressing yields the “after-wines.” The residue or “marc” (German, *Treber* or *Trester*) is sometimes treated with water to yield an inferior wine.

1,000 parts of ripe grape juice (must) contain, on an average :—

Water	-	-	-	-	-	860-830 parts
Sugar (dextrose and laevulose)	-	-	-	-	-	150-300 „
Pectin, gums, colouring matter, albuminous matter, etc.	-	-	-	-	-	30-20 „
Ash	-	-	-	-	-	2.7-4 „

100 parts of the ash contain :—

Phosphoric acid	-	-	-	-	-	16-14 „
Potash	-	-	-	-	-	64-71 „
Magnesia	-	-	-	-	-	5-2.5 „

**Fermentation of the Grape Juice.**—The grape juice begins to spontaneously ferment within a few hours owing to the rapid development of wine yeasts. These



occur on the grape skins and stalks. They find their way naturally into the juice, and there rapidly develop, since the must contains a considerable amount of nitrogenous proteid matter and mineral salts which serve as an excellent food for the developing cells. In the more southern countries the fermentation proceeds between  $15^{\circ}$ - $30^{\circ}$  C. and is a **top fermentation**. Along the Rhine and in colder countries usually a **bottom fermentation** takes place at  $10^{\circ}$ - $12^{\circ}$  C. in special wine cellars. As in the case of beer, the higher the temperature of fermentation the more rapidly it takes place; the best products, however, are obtained at moderate temperatures.

The yeasts (see **Wine Yeasts**, p. 230) consist of various races of *Saccharomyces ellipsoideus*, and, naturally, those races which resist best a high alcohol and acid content come to the front and overpower inferior races.

For many years **pure wine yeast** culture has been introduced into the wine industry. Wortmann proved that different **wine yeast** types yield very different products as regards taste, bouquet, and acidity. Nevertheless, the taste and bouquet depend very much upon the type of grapes, the soil, degree of ripeness, etc. etc. Pure cultures of the yeasts are always made from types found on the native grapes and in the resulting wines.

Excellent results with pure cultures have been obtained by Wortmann in the manufacture of **sparkling wines** (see **Champagne**), the isolated races producing very little turbidity and depositing as sediment on the cork. A pure culture for the production of sweet wines has been introduced with success by *Seifert*. These cultures are distinguished by their resistance towards a high alcohol and sugar content. Owing to the great variability of wine yeast types and the extreme shortness of the season of wine fermentation, the wine yeasts are not cultivated in large apparatus as in the brewing industry, but only in small quantities in special institutes, e.g., in Germany in the *Staatlichen Versuchsanstalt zu Geisenheim*. The wine manufacturer propagates his yeast in about 12 l. (3 gals.) of pure boiled **must**, and when this is in a vigorous state of fermentation, adds it to the bulk of his **must**. This latter must *not* be previously sterilised by boiling; as a rule, this occasions no inconvenience, for the added yeast develops so rapidly that it overcomes and suppresses not only undesirable wild yeasts, such as *S. apiculatus*, but also equally dangerous bacteria, especially acetic acid bacteria. Pure culture wines also clarify quicker and better than ordinary wines, and the bouquet of the young wine is generally better.

**The Principal Period of Fermentation** lasts three to fifteen days, and sometimes longer. The fermentation takes place in large casks or butts, the bung of which usually remains open. A little air is required; much air causes the development of acetic acid bacteria and the souring of the wine. The half-fermented wine (and also the **must**) is often consumed locally early in November, especially in the Rhine districts. The fluid in this condition, however, will not keep, and must undergo a further period of fermentation. Consequently as soon as the first vigorous fermentation is over, an "**after-fermentation**" is allowed to take place for several months. If the wine is "white wine," the cask is now filled to the bung with young wine and allowed to stand in the cask in which fermentation has taken place. If the wine is **red**—i.e., if the fermentation has been allowed to proceed in the presence of the grape skins until their colouring matter has partially passed into solution—the wine is at this stage drawn off from the grape skins and run into other casks and loosely bunged.

During this after-fermentation a sediment settles at the bottom and sides of the cask, consisting principally of potassium hydrogen tartrate (tartar) and yeast cells. The tartrate gradually crystallises out of the solution. This residue, called "**wine lees**," is worked up for tartaric acid (which see).

**Storing and Ripening of Wine.**—When almost all the sugar in the young wine has fermented into alcohol and carbon dioxide, and the liquid has stood until clear, the young wine is run off into large oaken wine-butts, tightly bunged up, and allowed to "ripen" in a cool cellar. This "ripening" is a very important process, making the wine drinkable, and giving it its characteristic "bouquet" and taste. The wooden walls are porous, and a small amount of oxygen filters in, while at the same time alcohol passes out and evaporates away from the wood. The volume of wine, therefore, slightly diminishes, and an air-space is formed over the liquid in the cask. If the air-space becomes too large it must be filled in,



otherwise fungi will develop. In order to diminish this loss of wine by evaporation attempts have been made to replace the wooden casks by non-porous vessels, made of glass or cement; but such receptacles have always proved quite unsuitable.

The bouquet is now gradually formed out of three different classes of substances: (1) from pleasant smelling and tasting substances originally present in the grape; (2) from similar substances formed during the period of fermentation by the vital activity of the yeast; (3) from wine-fusel oils, which are higher alcohols and by-products of fermentations.

The various alcohols and organic acids present gradually unite during the period of storage, and form pleasant smelling and tasting esters. The wine, however, does not continue to indefinitely improve with storage. It reaches an optimum, and then begins to deteriorate in taste, for the esters continue to increase while the alcohol content diminishes. Very old wine has a decidedly unpleasant, oily, sour taste. The ripening is sometimes accelerated by repeatedly drawing off the wine from one cask into another, and thus aerating it (Racking).

During this period of ripening a turbidity appears in the wine, due to precipitating albuminous substances and yeast cells. Before the wine can be bottled it must be clarified in such a manner that, once bottled, it remains clear. This is achieved by adding "finings," consisting of white of egg, gelatine, isinglass, ox blood, milk, or casein. These substances coagulate, and either sink to the bottom of the vessel, carrying with them all suspended matter, or rise to the surface, and are expelled through the bung hole. A better method of *fining* is to use a soluble sodium compound of *casein* (p. 79), dissolved in 10-20 parts of water. No flavour, precipitation complete.

"Plastering," or the addition of gypsum to the must, is said to improve the colour of red wines; the gypsum combines with part of the water, and increases the relative proportion of alcohol; this retards the fermentation and gives a longer time for the extraction of the colouring matter. Hence the improvement in colour. The calcium sulphate converts the soluble potassium salts into insoluble lime salts and potassium sulphate. Wine thus treated, therefore, not only contains gypsum but also potassium sulphate, and a considerable percentage of sulphates has injurious effects on the human organism. For this reason the addition of gypsum to wine should be condemned.

**Diseases of Wine.**—Wine is subject to several serious defects or maladies; among these we may mention: (1) The formation of *Mycoderma vini*, which occurs as a growth covering the wine after moderate exposure to the air. It destroys the flavour and renders wine flat. (2) The growth of *Mycoderma aceti*, which turns wine into vinegar. The acetic acid in normal wine should not exceed 0.2 per cent. (3) **Bitterness** due to various mould organisms and bacteria. All red wines are very liable to this disease. (4) The growth of the mould *Oidium vini*, which results in a mousy smell and the destruction of colouring matter. (5) **Ropiness or viscosity**, caused by the growth of organisms such as *Pediococcus acidi lactici*, *Bacillus viscosus*, etc. The wine becomes so viscous that it can be drawn out like birdlime. The disease is due to the decomposition of the remaining sugar into mannite and mucilage. It develops in wines deficient in tannin and alcohol. (6) **Foulness**—the development of an unpleasant smell, due to the formation of  $H_2S$ , mercaptans, etc. Due to the presence of too much sulphur in the wines; it may be produced by the excessive use of sulphur as an antiseptic, or by an excess of albuminoid matter in the wine. Storage at too high a temperature is a frequent source of disease.

The best means of preventing the deterioration of wine is to preserve the most perfect cleanliness in all processes, apparatus, and vessels. In its initial stages the malady may often be checked by lowering the temperature of storage, or by running the wine into *casks* which have been thoroughly disinfected by burning sulphur in them or by rinsing with a concentrated solution of sodium bisulphite. The addition of other antiseptics, such as **salicylic acid** or **boric acid**, is reprehensive and in many countries illegal. *Pasteur* introduced the process of "**Pasteurisation**." The bottled wine is heated to 60° C. in special vessels. This kills the injurious fungi and does not harm the wine. A higher temperature than 60° C. destroys the fine taste. In many districts alcohol is added to wine, as a high percentage of alcohol confers stability.

**Improving Wines.**—Only the very best varieties of wines are consumed unchanged as they come from the wine producer. Almost invariably wines are **blended** or mixed with other wines, chosen in such a way as to neutralise their defects. Thus sour wines are blended with sweet, wines with a poor aroma are blended with wines with a rich fine bouquet, thin wines with full bodied, etc. etc.

The following chemical methods of improving the quality of **wine must** and **wines** are in use:—

(a) **Removal of Acidity.**—Excess of acid in a wine is very detrimental to



its flavour. Chaptal's method of reducing acidity is to add pulverised marble or pure calcium carbonate. 60 parts of free acid as a rule require 50 parts of calcium carbonate for neutralisation. If the acidity is due to tartaric and malic acid, the method is very successful, a part of the acid being precipitated as calcium tartrate, and the wine retains only a very small amount of the calcium salt.  $\text{CaCO}_3$ , however, is of no use in the case of acetic acid fermentation, since the calcium acetate formed is soluble and remains in solution.

Sugar of lime (slaked lime + sugar water, decanted from undissolved lime) and neutral potassium tartrate are also used for removing acidity. The latter combines with the tartaric acid to form potassium bitartrate, which settles as an insoluble salt on the sides of the vessel.

According to Gall, a normal **must** should consist of free acid 0.6 per cent., sugar 24 per cent., water 75.4 per cent. The total acid, calculated as tartaric acid, should be within the limits 0.4-1.5 per cent.

(b) **Addition of Sugar.**—Many wine **musts** are poor in sugar; this is especially the case in a wet or cloudy season. A good wine **must** should contain 20-24 per cent. of sugar, and when deficient in this it is often the custom to add to the **must** the proper amount of **invert sugar** to bring it up to the standard. The addition of **starch sugar** (glucose) is not suitable, and is illegal in many countries. It has been found that 15 per cent. of sugar in the **must** produces 7.5 per cent. of alcohol in the prepared wine. Consequently the amount of sugar to be added, when the acid is in excess, is 2 parts for each 1 part of additional alcohol required in the finished wine.

(c) **The Addition of Alcohol.**—The presence of a high percentage of alcohol in wine makes it stable. For this reason, Madeira, Sherry, Port, etc., before export have usually alcohol, in the form of brandy or spirits, added to them in such a quantity as to raise the alcohol content to over 20 per cent. Although certain wine yeasts are capable of completely fermenting a 30 per cent. must, yet it may be taken as a rule that wines containing more than 15-17 per cent. of alcohol have had alcohol added to them.

From what has been said above it will be seen that the value of a wine *increases* with the amount of alcohol contained in it, and *diminishes*—within certain limits—with the amount of acid.

**Chaptal's Method** (1800) of improving wines and wine **musts** was (a) to neutralise the excess of acid with marble (50 marble to every 60 of acid); (b) to add sugar to the must in quantity sufficient to render the must normal, and thus restore the amount of alcohol to its proper amount in the finished wine (2 parts of invert sugar for every 1 part of alcohol required).

**Gall's Method** is to (a) reduce the amount of acid by diluting the must with water; (b) to add the proper amount of invert sugar to render the **must** normal.

An example will make this clear: Suppose a grape **must** contains 10 per cent. of sugar and 2 per cent. of acid. To make it normal we should require the addition of sugar and water to it in such amount as to reduce the acid to (say) 1 per cent. and increase the sugar to (say) 20 per cent. Since 2 parts of acid are contained in 100 parts of **must**, we should dilute the volume to 200 in order to reduce the percentage of acid in it to 1 per cent. Then 200 parts of the diluted must contain only 10 parts of sugar. Hence to raise the percentage of sugar to 20 per cent., we add to it 30 parts of sugar. The must would then contain 20 per cent. sugar and 1 per cent. acid. It should be noted, however, that in the different countries there are different legal limits to which the dilution may be carried. Thus in Germany water may only be added in quantity sufficient to reduce the **extract** to 1.6 per cent. in the case of **white wine** and 1.7 per cent. in the case of **red wine**.

**Petiot's Method** is based on the fact that the colouring and bouquet constituents remaining in the grape skins (marc) after the removal of the must are sufficient in amount to impart the colour and flavour of wine to a solution of sugar. The method, in fact, is an attempt to obtain a wine without the aid of **grape juice**. To the pressed grapes (marc) cold water is added in amount equal to the removed **must**, and the whole allowed to mix during two to three days, during which time the water takes up the various soluble constituents of the marc. The liquor is now pressed off, and the amount of sugar and acid it contains is determined. There is usually only 2-3 per cent. of sugar. Consequently an addition of 17-20 per cent. of sugar is made to render the must normal. If there is too little acid, **tartaric acid** is added to approximate to the acid contents of a normal **must**.



The artificial must thus obtained is then fermented in the usual way; while the grape skins are again treated as before, a longer immersion, however, being now made. The resulting wines are usually darker in colour than natural wines, and contain much tannin. They are usually artificially flavoured. Petiot's method is used in France, but is illegal in Germany.

**Freezing Wines** is employed for the purpose of reducing the aqueous contents, the water freezing out first, leaving an alcohol-rich fluid behind. When wine is cooled to  $0.6^{\circ}\text{C.}$ , a precipitate of potassium tartrate, nitrogenous substances, and colouring matter is formed. When this precipitate is removed, the wine, enriched in alcohol, is not liable to after-fermentation, and can be kept in vats and half empty casks.

Scheele adds glycerol (limits 1-3 l. per 1 hl. of wine) to wine.

### Different Kinds of Wines

**Effervescing Wines—Champagne.**—The bulk of champagne comes from France (1903, 35 million bottles; Germany produced in 1904 about 11 million bottles). The method of manufacture is as follows: Only best quality grapes are used, and the juice is expressed as rapidly as possible in order to prevent the wine taking colour from the grape skins. The juice from the second or third pressings is used for making inferior or red-tinted effervescing wines. The expressed juice is allowed to stand twenty-four to thirty-six hours in vats, whereby any earthy matter, etc., is deposited. The juice is then run into the fermenting tanks and allowed to ferment for about fifteen days. It is then put into securely bunged casks, sometimes with the addition of brandy (1 bottle to 100 bottles of juice). At Christmas the wine is fined with isinglass, and again in February. In April the wine is bottled. It should contain 16-18 per cent. sugar, 11-12 per cent. alcohol (by volume), and free acid *equivalent* to  $0.3-0.5\%$   $\text{H}_2\text{SO}_4$ . Before bottling it is mixed with 2 per cent. of pure cane sugar in solution and some yeast, securely corked, allowed to ferment again at  $24^{\circ}\text{C.}$ , and then allowed to lie horizontally in bins for one to two and a half years. The bottles must be specially strong and without flaw, for the pressure of the  $\text{CO}_2$  in them rises to 5-6 atmospheres. Nearly 5 per cent. of the wine is lost by the bursting of the bottles. During the summer a deposit of yeast is gradually formed. In the following winter this is removed by placing the well-cooled bottles mouth downwards in special shaking machines and shaking repeatedly, when the deposit settles on the cork. The cork is opened for a moment, when the yeast is instantly shot out; a quantity of liquor, consisting of a solution of sugar in cognac, is now rapidly added, a new cork inserted and securely wired on. If the wine is still not clear the process must be repeated. The last lot of sugar added does not ferment owing to the absence of yeast. The wine must be perfectly clear. The carbon dioxide is chemically combined in the fluid, and should slowly escape from the cooled wine in small "pearls." The composition of sparkling wines varies widely. The following are typical analyses:—

Parts of Wine Contain.	Sample 1.	Sample 2.
	Per Cent.	Per Cent.
Free acid (counted as $\text{H}_2\text{SO}_4$ ) - - -	0.53	0.78
Alcohol - - - - -	8.40	9.80
Sugar - - - - -	4.30	9.10
Extractive matter - - - - -	7.50	15.20
Specific gravity - - - - -	1.029	1.041

All wines are capable of being produced as effervescing wines if the bottling is performed before the fermentation is over; for the carbonic acid is retained in the wine, and, on opening, the rapid disengagement of gas causes effervescence. Not only genuine champagnes, but also Hocks, Moselles, and red wines, may be thus treated with good results. If the wine contains much sugar, the fermentation is



arrested in the bottle before all the sugar is consumed, and the result is a sweet effervescing wine. If, however, the sugar is all exhausted in producing  $\text{CO}_2$  and alcohol, dry effervescing wine is produced. Dry effervescing wines usually agree better with the digestion than sweet wines.

Cheap imitation champagnes and sparkling wines are now manufactured by pumping in  $\text{CO}_2$  under pressure. They usually become turbid on keeping, and the  $\text{CO}_2$  in them is not so stably bound as in genuine champagnes.

Most **Sweet Wines, Dessert Wines, and Medicinal Wines** are *artificial products*. In other words, they are not obtained by the natural process of fermentation of fresh grapes, but more or less alcohol or sugar is added. The best-known types of sweet wines are: Tokay, Port, Sherry, Madeira, Malaga, etc.

**Tokay** is obtained from ripe grapes which have been allowed to partially dry, either on the vine tree itself, or on **straw** after plucking, so that the sugar is unable to completely ferment.

**Port Wine** is obtained by fermenting the must down to 6-8 per cent. of sugar, and then 4-7 per cent. of alcohol is added to arrest further fermentation. The wine then contains 14-15 per cent. of alcohol. In the spring the wine is racked, and 2-3 per cent. more alcohol added. The final product contains 20-24 per cent. of alcohol. By suitable "blending," the best results are obtained.

**Sherry Wine** is made from several varieties of white grapes of Andalusia, Spain. After each pressing of the grapes the wine is "plastered" with gypsum. The must is fermented to 8-10 per cent. sugar, and alcohol is added to bring the percentage up to 16-18 per cent. Sherry wine is usually ripened by "baking" the wine by natural or artificial heat. The filled wine casks are placed in tiers in a building with roof and side of glass. The temperature in the sherry house is as high as  $60^\circ \text{C}$ ., and at night time is maintained by fires.

**Different Kinds of Wines.**—The following is a list of the best-known wines, arranged according to the country of production:—

1. **French Wines.**—Barsac, Burgundy, Chablis, Champagne, Claret, Frontignac (Muscat), Graves, Hermitage, Medoc, Roussillon, Saumur, Sauternes, etc.
2. **German Wines.**—Riesling, "Rhine," "Moselle," and "Pfalz" are applied to wines made in the respective districts. "Hock" is also the name of certain Rhine wines.
3. **Italian Wines.**—Asti, Barbera, Barolo, Capri, Chianti, Falerno, Lacryma Christi, Marsala, Muscat of Syracuse, Nebbiolo, Valtellina, etc.
4. **Austria-Hungarian.**—Ausbruch, Goldeck, Tokay, Vöslauer.
5. **Spanish.**—Malaga, Sherry, Val de Penas, Vinos Tintos.
6. **Portuguese.**—Carcavellos, Collares, Lisbon, Ports.
7. **Madeira and Canary Islands.**—Canary (sack), Madeira, Malmseys, Malvasia.
8. **Swiss.**—Gringet, Montreux, Neuchâtel.
9. **Greek.**—Corinth, Hymettus, Kephisia, Noussa, Patras, Santorin, etc.
10. **Turkish.**—Candian (Crete), Cyprus, Mt. Lebanon, etc.
11. **Russian.**—Crimean, Donski, Kakhétian (Caucasus), Krimshi.
12. **Persian.**—Shiraz.
13. **Australian.**—Australian Burgundy, Hermitage, Port, Sauterne, etc.
14. **South African.**—Cape Madeira, Constantia.
15. **American.**—Californian Port, Champagne, etc.

**Alcoholic Strengths of Wines.**—These vary somewhat. The following numbers are typical:—

	Specific Gravity.	Alcohol per Cent. by Volume.		Specific Gravity.	Alcohol per Cent. by Volume.
Burgundy -	0.9913	10.5	Port (natural) -	0.9992	14.5
Champagne -	1.0109	10.4	,, (fortified) -	...	21.5
Claret -	0.9950	9.6	Rhine -	0.9928	10.2
Marsala -	0.9959	16.0	Sherry -	0.9859	16.0



**Wine Production of the World.**—The following figures show the quantity of wine produced by the leading wine-producing countries of the world for the year 1909.

### VINTAGE FOR 1908 AND 1909

Country.	Hectolitres.	Hectolitres.*	Country.	Hectolitres.	Hectolitres.*
	1908.	1909.		1908.	1909.
France - - -	60,545,265	54,445,860	Russia - - -	2,800,000	2,400,000
Italy - - -	47,868,000	41,398,000	Germany - - -	3,135,953	1,900,000
Spain - - -	18,556,717	14,767,911	Greece - - -	2,800,000	2,200,000
Algeria - - -	7,803,734	8,228,719	Turkey and Cyprus	1,800,000	1,500,000
Austria - - -	8,399,964	4,500,000	Argentina - - -	1,250,000	1,100,000
Portugal - - -	3,900,000	3,100,000	United States - -	1,197,951	1,500,000
Hungary and neighbouring lands	5,500,000	1,925,000	Switzerland - -	1,200,000	1,010,000

\* 1 hectolitre = 1,000 litres = 220.1 gallons.

The English *import* of wine in 1910 reached 13,735,000 gals., value £4,249,000. The *export* was 798,000 gals., value £468,000. The United States in 1910 imported \$6,300,000 champagne and \$6,605,000 still wines. The export was \$225,000. California produced 130,000,000 gals.; State of New York, 22,000,000 gals.; Ohio, 17,600,000 gals. Invested capital, \$100,000,000. For statistics regarding **Mineral Waters, Fruit Wines, etc.**, see p. 250.

For modern statistics see Appendix III.

## FRUIT WINES, ETC.

### LITERATURE

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Wine is usually prepared from grape juice merely because it is the richest in sugar, contains pleasant-tasting organic acids, and the fermentation is easy to carry out; moreover, the product is very stable. Nevertheless the juices of other fruits, such as apples, pears, gooseberries, currants, elderberry, figs, rhubarb, etc., can also be fermented, and if sugar is added to the juice until it contains about 20 per cent., excellent wines may be obtained. Sometimes nitrogenous food stuffs must be added to the juice to cause the yeast to properly grow.

In **Germany, France, and England** a considerable amount of cider (“apple-wine”) is produced by the fermentation of apple juice. France produces nearly 20,000,000 hl. of cider yearly. Cider is distinguished from grape wine by the absence of tartaric and citric acids. It may contain 5-6 per cent. of alcohol. If a moderate proportion of tartaric acid is added to cider the product cannot be distinguished from wine. In gooseberry, currant, and other fruit wines tartaric and citric acids are usually absent.

**Palm Wine** is fermented juice of the sugar palm, and is largely consumed in tropical countries.

**Saké** is an alcoholic drink made from rice by the Japanese and Chinese. The rice is saccharified by means of the mould *Aspergillus oryzae* (see pp. 226, 286), and the liquid fermented by another yeast mould called “Mots.” Saké contains 10-15 per cent. of alcohol and little extract or CO<sub>2</sub>.

**Aerated and Mineral Waters (Artificial)** are made by forcing carbonic acid gas into water (best distilled) in which various salts and flavouring matters are dissolved. Saturation with CO<sub>2</sub> is usually carried out under 5 atmospheres pressure, the CO<sub>2</sub> being now usually supplied in a liquid form in steel cylinders. At one time—and to some extent at present—special apparatus were employed



in which the  $\text{CO}_2$  was generated, the generators being usually of copper internally coated with lead or earthenware, and the  $\text{CO}_2$  was obtained by the aid of  $\text{HCl}$  or  $\text{H}_2\text{SO}_4$  on marble, chalk, magnesite, etc. The gas is always purified by passing through (a) water, (b)  $\text{NaOH}$ , (c)  $\text{FeSO}_4$  and  $\text{NaHCO}_3$  (to remove  $\text{H}_2\text{S}$ ), (d)  $\text{KMnO}_4$ . For the apparatus employed see the special works below referred to.

**Lemonades** contain sugar, citric, or tartaric acid and sometimes scents. Ordinary "**Seltzers**" consists of cryst.  $\text{Na}_2\text{CO}_3$  (25) +  $\text{NaCl}$  (5) +  $\text{Na}_2\text{SO}_4$  (cryst.) (6) + 10,000  $\text{H}_2\text{O}$ . **Apollinaris** = 217  $\text{NaHCO}_3$  + 4.5  $\text{NaCl}$  + 2.8  $\text{Na}_2\text{SiO}_3$  + 29  $\text{CaCl}_2$  + 42.8  $\text{MgCO}_3$  + 16.7  $\text{MgSO}_4$  + 3  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  + 1.7  $\text{HCl}$ , all dissolved in 100,000 water.

The finished waters usually contain  $\text{CO}_2$  under a pressure of  $1\frac{1}{2}$ -2 atmospheres.

**Literature.**—SULZ, "Beverages" (New York, 1888); KIRKBY, "Artificial Mineral Waters" (Manchester, 1902); TENIM, "Limonaden u. alkoholfrein getranke" (Vienna and Leipzig, 1909); FRITSCH, "Eaux et Boissons gazeuses" (Paris, 1906); HIRSCH-SIEDLER, "Künstlichen Mineralwässer" (Braunschweig, 1897); HERMANN-LACHAKELLE, "Boissons gazeuses" (Paris, 1891); GOOLD, "Aerated Waters" (London, 1881).

**Statistics.**—England imported in 1910: Aerated and mineral waters, 1,694,000 dozen bottles, value £341,000; cider and perry (sugar free), 261,000 gals., value £8,000; wine, 13,735,000 gals., value £4,249,000.

The export in 1910 was: Aerated and mineral waters, 1,438,000 dozen bottles, value £235,000; wine, 798,000 gals., value £468,000. The United States in 1910 imported: cherry juice and other fruit juice, 38,000 gals. (value \$27,000); prune juice, 24,000 gals. (value \$18,000); cider, 8,000 gals. (value \$8,000); lemonade and soda water, 66,000 doz. pints (value \$55,000). The United States export of cider sank from 344,000 gals. (value \$54,000) in 1906 to 6,000 gals. (value \$2,000) in 1910. The export of fruit juice was \$52,000 in 1906 and \$85,000 in 1910. Only \$2,000 of mineral waters were exported in 1910.

For modern statistics see Appendix III.

## Chemical Analysis of Wine

For details readers should consult the special works mentioned above, especially the article on "Wines and Potable Spirits" in Allen's "Commercial Analysis," vol. i. (1909). The following is a summary of the methods employed:—

1. **Alcohol Percentage.**—The natural wines contain 7-12 per cent., seldom over 15 per cent. Certain Spanish and Portuguese export wines, e.g., Port, contain 20-23 per cent. ("Fortified" wines). The alcohol is determined by distillation. 50 c.c. of wine are mixed with 25 c.c. of water and distilled until 50 c.c. of fluid has passed over. The alcohol is determined in the distillate by taking its specific gravity by means of the Pyknometer ( $15^\circ \text{C}$ .), and then using special tables (e.g., Windisch's).

2. **Extract** is the substance which remains behind on evaporating the wine to dryness on the water bath. In natural wines it amounts to 1.8-2.5 per cent., and should never be less than 1.6 per cent. It is determined by evaporating 25 or 50 c.c. of wine to dryness, first to a syrup on the water bath and then for two hours in the steam oven. Also from the specific gravity of the original wine and of the alcoholic distillate. If  $S$  = specific gravity of the wine, and  $S'$  = specific gravity of alcoholic distillate (see 1), then percentage extract (in grams per 100 c.c.) =  $(S - S') \div 0.00386$ .

3. **Sugar.**—Ordinary dry wines contain very little sugar, but sweet wines often contain several per cent., usually as invert sugar. The amount of invert sugar is obtained in the usual way by Fehling's solution, the wine being first neutralised with  $\text{NaOH}$  and decolourised by basic lead acetate solution. The cane sugar is determined by hydrolysing 50 c.c. of the clarified and neutralised wine with  $\text{HCl}$ , and then estimating by Fehling's solution. The total titration, less than that due to the invert sugar, gives the amount of cane sugar. The amount of impure starch sugar (which is accompanied by dextro-rotatory non-fermentable dextrine) is found by fermenting it and taking the specific rotation. For details see Allen's "Commercial Analysis."

4. **Free Acids.**—Reckoned as free tartaric acid, the total free acids usually amount to 0.4-1.0 per cent. of the wine. In France it is customary to calculate the acidity as equal to so many grams of sulphuric acid per 1,000 c.c. To determine the acidity the hot liquid is rapidly titrated with  $\frac{N}{2}$   $\text{NaOH}$ , using litmus paper as indicator. The Volatile acids, which, counted as acetic acid, amount to 0.1-0.2 per cent., is determined by distilling 50 c.c. of the wine in a current of steam free from  $\text{CO}_2$  and titrating with  $\frac{N}{10}$   $\text{NaOH}$ , using phenolphthalein as indicator. The total amount of tartaric acid present is found by precipitating with potassium acetate and alcohol.



5. **Mineral Salts.**—Wines seldom contain less than 0.15 per cent. of mineral salts. Wines on the average contain about 0.1 per cent. of  $K_2SO_4$ . More than 0.2 per cent. is held to be evidence of "plastering," *i.e.*, the addition of gypsum to the must. In Germany and France wines containing more than 0.2 per cent  $K_2SO_4=0.092$  per cent.  $SO_3$  are *illegal*. In France wines must not contain more than 0.1 per cent.  $NaCl$ .

6. **Sulphurous Acid** must not in France and Switzerland exceed 200 mg. per 1,000 c.c. Free sulphurous acid must not exceed 30-20 mg. per 1,000 c.c.

7. **Glycerol** lies, usually, between 0.4 and 1 per cent., sometimes 0.16-1.4 per cent.

8. **Foreign Colouring Matters.**—Coal-tar colours are usually detected by boiling cleaned wool (previously mordanted with alum and sodium acetate) with wine. The foreign colours are precipitated on the wool and are examined by the usual reagents. Coal-tar colours are also detected by the **lead acetate** test (see Allen), by Cazeneuve's mercuric oxide test, by extracting with ether before and after supersaturation with ammonia, and by extracting with amyl alcohol. The artificial addition of bilberry or other fruit juices—which contain natural colouring matters very similar to that in grape skins—is, however, very difficult to detect.

**Brandies from Wine.**—These are obtained either by directly distilling the marc (fermented grape skins) or second wines derived from it. The best kinds of brandy, "cognacs," are obtained by distilling good wine. The wash for brandy spirits is obtained by running water into a tank filled with the mash, the overflow running into other similar tanks. The fluid is distilled when it contains over 5 per cent. alcohol. See under **Spirit Manufacture**.

**Wine Fusel Oils** vary very much in composition, according to the nature of the must, their fermentation and storage. They occur in wines, but also, and to a far larger extent, in genuine cognacs (obtained by distilling wine). Of the following samples the first was obtained by distilling an old cognac, while the second was obtained from the fermentation of a cane sugar solution with wine yeasts:—

COMPOSITION OF WINE FUSEL OILS (after *Ost*)

1. IN 100 L. COGNAC.	2. FROM 100,000 G. CANE SUGAR.
Normal butyl alcohol - - - 218.6 g.	Alcohol - - - - - 50,600 g.
Amyl alcohol - - - - 83.8 "	Glycerol - - - - - 2,100 "
Normal propyl alcohol - - - 40.0 "	Succinic acid - - - - 452 "
Ethyl acetate - - - - 35.0 "	Acetic acid - - - - 205 "
Acetal - - - - - 35.0 "	Isobutylene glycol - - - 158 "
Esters of fatty acids - - - 7.0 "	Amyl alcohol - - - - 51 "
Acetaldehyde - - - - 3.0 "	Normal propyl alcohol - - - 2 "
Heptyl alcohol - - - - 1.5 "	Isobutyl alcohol - - - - 1.5 g.
Hexyl alcohol - - - - 0.5 "	Esters of organic acids - - - 2.0 "
Amine bases - - - - 4.0 "	

The wine fusel oils are either obtained by the fractional distillation of fermented grape skins or wine lees (marc), when they are known as "cognac oil," or "grape oil." They are sometimes artificially made for adding to brandies and cognacs (see p. 384). It will be noticed that they are entirely different in character to the fusel oils obtained from whisky or potato spirit manufacture (see under **Spirits**, pp. 312, 298).

## IV.—BEER

BY C. H. GRIFFITHS AND G. MARTIN, Ph.D., D.Sc.

## LITERATURE

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Beer is an alcoholic beverage obtained from malt, hops, and water. It differs from wine and spirits in containing less alcohol (3·6 per cent.) and being richer in extracts (4·8 per cent.).

**Statistics Relating to Beer.**—The following numbers show the production of beer in the principal countries of the world, and also the amount of beer consumed per head of the population. It will be seen that the United States is now the greatest beer-producing nation (*Os!*):—

Country.	Production in Millions of Hectolitres.*	Consumption per Head of the Population in Litres.
United States (1909) - - - - -	66·0	70
Germany (1909) - - - - -	64·8	100
England and Ireland (1907) - - - - -	58·3	126
Austria (1908) - - - - -	20·4	73
Belgium (1908) - - - - -	14·0	210
France (1905) - - - - -	13·7	35
Russia (1904) - - - - -	6·2	5
Italy (1905) - - - - -	0·24	1

\* 1 hectolitre = 100 litres = 22·01 gallons ; 1 barrel = 36 gallons.

In 1908-09 in the *United Kingdom* there were 4,667 breweries ; these produced 34,953,274 barrels. The duty levied on each barrel of beer was 7s. 9d., the total revenue raised being £13,144,445. The amount of material used in 1908 for brewing in the United Kingdom was :—

Malt, 50,960,923 bushels.  
Unmalted corn, 91,069 bushels.  
Rice, maize, flaked rice, etc., 1,278,988 cwt.

Sugar, including its equivalent of syrup, glucose, and saccharum, 2,883,269 cwt.  
Hops, 62,971,755 lbs.  
Hop substitutes, 4,479 lbs.



In Germany (*Norddeutschen Brausteuergebiete*) during 1909 the following quantities of raw products were used in brewing 38.4 million hectolitres of beer:—

Barley malt -	-	-	-	-	-	6,650,000 dz.*
Wheat malt -	-	-	-	-	-	94,200 „
Rice (raw) -	-	-	-	-	-	83,300 „
Sugar and (little) syrup and other malt substitutes -	-	-	-	-	-	47,200 „

The largest German brewery (Schultheiss) used in 1909 no less than 240,000 dz.\* malz.

Within recent years small firms have been steadily diminishing and large ones increasing. In 1874 there were in the United Kingdom no less than 34,000 breweries, whereas now the number is 4,667. The largest breweries are: Guinness & Co., Dublin (over 2,000,000 barrels), Bass, and Allsopp, in Burton-on-Trent (the first having a yearly output of between one and two million barrels). In 1899 the amount of capital invested in breweries in the United Kingdom was over £240,000,000, and is considerably in excess of this figure to-day.

On the Continent the largest breweries are: Dreier in Kl. Schwechat-Wien, Schultheiss in Berlin (1,000,000 hl.). München yields 3,000,000 hl.; the largest brewery in the town being the Löwenbrau (320,000 barrels). In Northern Germany, each hectolitre (100 l. = 22.01 galls.) has to pay a duty of 2.4 m. (1909), and in Bayern, 4.8 m. The total revenue derived from this beer duty for the whole German Empire was in 1909 154,000,000 m. (20 m. = £1).

The capital invested in the American brewing industry in 1909 was \$671,158,000, being an increase of 30 per cent. in five years. The value of products was \$374,730,000 in 1909. The number of breweries was 14,100. The average capital per establishment was \$475,000 in 1909 against \$337,000 in 1904. 223 breweries in 1910-11 were equipped with pipe lines for conveying beer to the bottling premises. The duty paid for ale, beer, lager beer, porter, etc., for 1910-11 was \$63,216,851. The total production of malt liquors in 1910-11 was 63,283,000 barrels, against 40,517,000 barrels in 1901-02.

**Outline of the Theory of Brewing.**—Most corn grains consist of about 60-65 per cent. of starch, a complex hydrocarbon of the constitution  $(C_{12}H_{20}O_{10})_{20}$  (Brown and Morris). Starch, however, will not undergo alcoholic fermentation. It must first be broken down into simpler carbohydrates. This is achieved by allowing the grain to germinate (malting). During the process of malting the enzyme **diastase** is formed. This is capable of attacking the starch, breaking it down into the sugar **maltose**,  $C_{12}H_{22}O_{11}$ , and into dextrin  $(C_{12}H_{20}O_{10})_{20}$ . The diastase is soluble in water, and acts best between 40°-60° C. Consequently the germinated grain (malt) is crushed or ground and mixed with hot water ("mashed") in order to let the diastase act freely on the starch. This it does, the bulk of the starch being rapidly converted into maltose. The solution is now boiled to destroy the diastase, and yeast is added. This, and also malt, contains an enzyme called **maltase** which rapidly decomposes the maltose,  $C_{12}H_{22}O_{11}$ , into 2 molecules of the simpler sugar, dextrose,  $C_6H_{12}O_6$ :  $(C_{12}H_{22}O_{11} + H_2O = 2C_6H_{12}O_6)$ ; then another enzyme contained in the yeast, Buchner's "Zymase," rapidly converts the dextrose into alcohol and carbon dioxide:  $(C_6H_{12}O_6 = 2C_2H_5OH + 2CO_2)$ . The resultant beverage is known as beer.

The grain used for conversion into malt is barley. Sometimes, however, other sorts of grain are mixed with the malt in the mashing process, the diastase of the malt being able to attack their starch.

From this short description it will be seen that the manufacture of beer naturally resolves itself into three distinct processes:—

1. The preparation of malt, *i.e.*, germinated barley.
2. The preparation of the wort, or fluid which is to be fermented. This stage of manufacture may be further divided into (a) the mashing process, or the mixing of the ground malt with hot water and its saccharification; (b) boiling and hopping the wort to destroy the diastase; (c) cooling the wort.
3. Fermentation of the wort and storage of the resulting beer. Each of these processes will now be described in detail.

## THE PRODUCTION OF MALT

**Raw Materials used in Brewing.**—Barley is the grain mostly used for making malt for lager beer, ale, stout, vinegar, and yeast makers' or distillers' mash, while wheat malt is used in Germany and U.S.A. in the production of Weiss-bier.

\* 1 dz. = 100 kg. = about  $\frac{1}{4}$  ton.



Commercial cultivated barley belongs to the genus *Hordeum*, and species *Hordeum sativum*. Four leading types or sub-species of barley are met with in commerce, viz. : \*—

1. *Hordeum distichum*.—These are *two-rowed barleys*, with a *narrow ear* and a comparatively long distance between the corns. Well-known varieties are: Chevalier, Kinver, Archer, Hallett, Hanna, Black and White Ocichæ.

2. *Hordeum zeocriton*.—These are *two-rowed barleys*, with a *wide ear* and a comparatively *short* distance between the corns. *Varieties*: Goldthorpe, Peacock, or Fan Barley. Standwell and Invincible are hybrids resembling Goldthorpe.

3. *Hordeum vulgare*.—These are *six-rowed barleys*, with *narrow ear* and a comparatively long distance between the corns. *Varieties*: Scottish "bere" or "bigg." Most "Light Foreign" six-rowed barleys are mixtures of white and blue *H. vulgare*.

4. *Hordeum hexastichum*.—These are *six-rowed barleys* with *wide ear* and short distance between the corns. *Varieties*: Chilian six-rowed barley is a mixture of white and blue *H. hexastichum*.

**Other Raw Materials.**—In Germany, as a rule, only malt is used for brewing. In America, however, and to a lesser extent in England, a considerable quantity of raw grain is mixed with the malt, especially maize or rice. Since the malt is very rich in diastase there is enough diastase present not only to saccharify the starch in the malt, but also that in the added raw grain. In Germany sometimes **rice** is mixed with the malt in making top-fermentation beer. The beer thus produced acquires a peculiar taste, and loses in stability.

In England and America, and to a small extent in Germany for special kinds of top-fermentation beer, various kinds of sugar, especially cane sugar, starch sugar (glucose), syrups, etc., are added to the malt. The complete fermentation of the pure sugars increase the amount of alcohol in the beer, leaving unaltered the amount of extract. Starch sugar and syrups, however, which contain non-fermentable isomaltose and dextrine, enrich the beer in extract. **Hops** are added to the beer to give it a bitter flavour and preserve it. The world's production of hops amounts to about 1,000,000 cwt. yearly, England importing about 200,000 cwt. (value about £800,000). The U.S.A. import in 1910 amounted to 3,200,000 lbs. (value \$1,500,000), while the export was 10,600,000 lbs. (value \$2,000,000). The hops used in brewing consist of the ripe female flowers of the *Humulus lupulus*, also *H. Americanus* and other varieties. Male flowers exist in English hop gardens because a bigger yield per acre is obtained. In Germany the presence of male hops is not tolerated. Unfertilised hops are finer. See Salmon, *Journ. Inst. Brewing*, 1917, xxiii., 60; 1908, xiv., 309.

The sticky yellow dust, known as "hop-flour" or "lupulin," attached to the lower inside base of the bracts of the hop cone, contains the resins, volatile oils, and bitter substances which are of value to the brewer. Hence hops are valued by their content of **lupulin** (hop flour), which may amount to 10-15 per cent. of the hops. The resins are acid in nature (lupulin acid, hop bitter acid), very soluble in ether, partly soluble in petroleum, and very sparingly soluble in water. They are divided into  $\alpha$ -,  $\beta$ -, and  $\gamma$ -resins, the first two resins being known as "soft resins," and contain the bitter and antiseptic substances which destroy bacteria, which otherwise easily multiply in unhopped beer. See, however, Power, Tutin, and Rogerson, *Journ. Inst. Brewing*, 1913, xix., 392; Brown and Clubb, *Journ. Inst. Brewing*, 1913, xix., 261.

The pleasant aroma given to beer by the hops is due to a volatile essential oil ("Hop oil"), amounting to 0.2-0.8 per cent. in good hops, and consisting of terpenes,  $C_{10}H_{16}$ , valeral,  $C_4H_9CHO$ , etc., etc. Hops, on keeping, lose their pleasant aroma owing to the conversion of the valeral into valeric acid,  $C_4H_9COOH$ . The **tannin** in the leaves of the hops is valuable in that it precipitates albumen and hence helps to clear the wort.

**Hops** are rendered preservable by drying in kilns and treating with  $SO_2$  fumes (sulphur being thrown on the fire of the drying kiln) and packed in sacks or zinc boxes in a cool place.

**Testing the Barley Grain.**—The barley, as bought in the open market, should be dry, heavy (55-56 lbs. to the bushel), even in size, pale yellow in colour, sweet in smell, with a thin skin. It should be rich in starch, but poor in nitrogen, free from broken grains, also few bacteria and moulds. It should be as free as possible from steely grains and have a good germinative power. The percentage of "steely grains" is usually determined by a simple instrument called a "**Farinator**." The corns to be tested are placed in a tray containing fifty holes; a slight shake fills each hole with

\* See E. S. Beaven, "Varieties of Barley," *Journ. Inst. Brewing*, 1902, viii., 547.



a grain; they are then cut with the knife crosswise, the result showing in a bottom tray containing fifty corns, so that the percentage of steely grains is easily counted.

The germinating power of the barley is usually tested by means of Coldewe's germinating apparatus, which consists of a glass half filled with water, above it the barley in the porcelain tray filled up with sand and covered with felt, above this is a wooden cover and the attached thermometer forms a handle. It is left in a warm cupboard or any convenient place, and in about ten hours the good grain will have sprouted. The tray holds exactly 100 corns, so that the percentage of idlers is seen at a glance (Fig. 97).

Should, in a particular sample, anything but an extremely small percentage (2-3) of the grains be incapable of germinating, good malt cannot be made from it. All ungerminated grains form breeding-grounds for mould during the malting process, and represent so much raw barley in the finished malt.

**Anatomy and Chemical Composition of the Barley Grain.**—The barley grain is very similar in structure to the wheat grain (Fig. 68, p. 179), consisting of two main parts:—

A (Fig. 98), the **Endosperm**, which consists principally of starch cells, surrounded by a husk *a*.

B, the **Germ**, from which the living plant develops.

Between A and B lies a cellulose membrane, *gg*, called the **scutellum**.

*c* is the **Plumule** or acrospire, *i.e.*, the part which, growing upwards, ultimately develops into the stalk and leaves of a new plant.

*d* is the radix or **Radicle**, *i.e.*, the part which, growing downwards, develops into the roots of the new plant.

The barley grain consists of 60-65 per cent. starch, which is contained in A, 12-18 per cent. moisture, 8-15 per cent. nitrogenous matter (principally in B), 7 per cent. cellulose and pentosane, 2.5 per cent. fat, 2.5 per cent. ash (very rich in  $P_2O_5$  and  $K_2O$ ).



FIG. 97.—Coldewe's Germinating Apparatus.

## Malting

**Theory of Malting.**—When barley is moistened and kept at  $10^{\circ}$ - $18^{\circ}$  C. for some hours it begins to germinate. When this occurs, Messrs Brown, Morris, and O'Sullivan have shown the enzymes diastase and cytase are producing in considerable quantity in the developing germ B (Fig. 98). The **cytase** dissolves the cellulose membrane *gg* which divides the starchy matter in the endosperm A from the germ B. The diastase can then gradually diffuse from *gg* into the starch in A. The diastase then breaks down the starch into various sugars, principally maltose, but also sucrose and invert sugar is produced. At the same time proteolytic enzymes, such as peptase, appear in the germ B, which hydrolyse the albumens first into peptones and later into amino acids. It is obvious, therefore, that with the process of germination a succession of very complex substances are formed by the developing germ. The germ breathes, absorbing oxygen (hence the practice of aerating malt) and throwing out  $CO_2$  and water, and generates warmth. The great mass of starch contained in the endosperm is, however, quite unaffected by the diastase and other enzymes, on account of the slowness of diffusion. In consequence, however, of the cellulose-dissolving action of the cytase enzyme the cell membranes become loose, and the barley grain becomes soft and is easily gelatinised by boiling water.

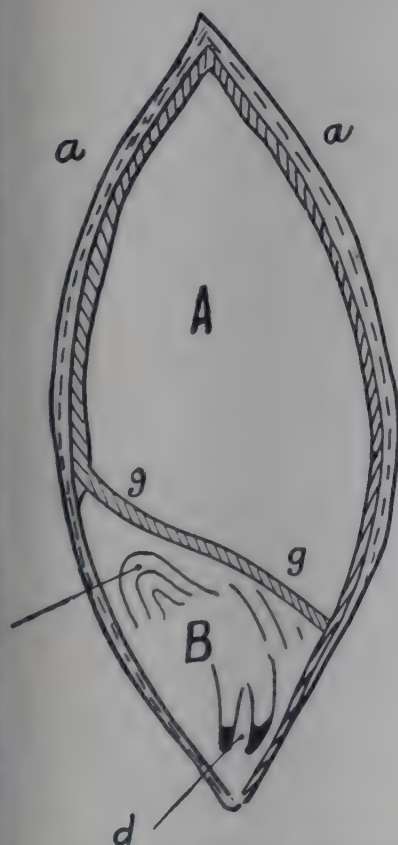


FIG. 98.—Rough Diagram of Longitudinal Section through a Barleycorn. (For greater detail see Section through a Wheat Grain, Fig. 68, p. 179.)

**Brown and Morris** have shown that the formation of diastase takes place principally in the epithelium (the fine membranous lining of the internal organs of the grain), and is favoured by the presence of small quantities of acid, but is almost completely restricted by readily assimilable sugars. Thus if barley be germinated in such a way that a sufficient quantity of cane sugar for the sustenance



of the embryo is always present, no diastase is formed, and it is therefore probable that the diastatic secretion of the epithelium is due to the stimulus of a starvation process.

**Growth of the Acrospire and Radicle.**—After moistening the grain or “steeping” for forty-eight hours, the **acrospire** grows upwards *under* the skin, while the **radicle** (roots) grows downwards.

The successive stages of growth are represented in the figure. *a* is the original grain, in *b* the process of germination is beginning, in *c* the roots are well developed,

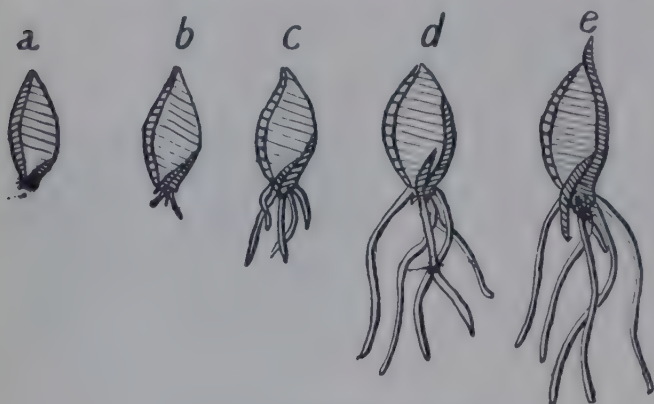


FIG. 99.—Growth of Malt.

and the acrospire has grown nearly half way up the grain. After about seven to eight days the acrospire will be three-quarters way up the grain, and the roots one to one and a half times the length of the corn. This is shown in *d*. When this stage is reached, the process of germination is stopped by heating on kilns.

The malt should never (in malting for beer) be allowed to germinate so long that the acrospire begins to emerge from under the skin at the top of the grain as shown

in *e*. It is true that the amount of diastase increases with growth beyond *d* up to a certain limit, but a growth beyond *d* causes the unnecessary destruction of much starch, and so is uneconomical. Consequently the brewer always works with “short malt” as the product is called. It should be noticed that a fairly low temperature favours the production of diastase, and is necessary for a good brewing malt. Moreover, the brewer always uses **Short Malt** (see p. 285), *i.e.*, malt germinated for a seven to ten day period, which contains sufficient diastase for his purpose, and a high percentage of starch. The *distiller*, on the contrary, works with “**Long Malt**,” *i.e.*, barley germinated for twenty days or so, for reasons that are explained under **Spirits** (pp. 285, 286).

### Practice of Malting in Relation to Brewing

In England the seasons during which malting is carried out is usually from about the middle of September until the middle of the following May, although where large quantities of foreign barley are dealt with, malting operations are often carried on throughout the whole year.

#### FLOOR SYSTEM OF MALTING

The system of malting most generally used in England is the **floor system**, which we will now describe:—

**Sweating the Barley.**—The best malt can only be produced by using a properly dried barley. This is often a matter of great difficulty, especially with English barleys and a wet harvest. Most maltsters, therefore, dry or “sweat” their barley before storing, in **kilns** at a temperature not exceeding 105° F.\* A space of 16 ft. per quarter is usually allowed in a kiln. Sometimes the sweating is done on the malt kilns between the stages of curing the malt (see p. 260), or on a specially built kiln, or by means of a drying drum (similar to the one shown for germinating barley, Fig. 107). This latter is a closed drum and is rotated by means of a worm and worm-wheel gear. At one end the drum is connected by means of a pipe to a furnace, and at the other end to a fan. The barley is put into the drum by doors in the walls or shell of same. The doors are then closed, the drum set in motion, and hot air from the furnace is sucked through the barley by the fan, which discharges its moisture-laden air into the atmosphere. The exact method to be employed in thus sweating the barley is a matter depending to a great extent upon local conditions.

The sweating process mellows the barley and gets rid of excess of moisture, thus inducing a more uniform absorption of moisture in steeping. Sweated barley should not be steeped within a fortnight of sweating. It does not heat in bins.

\* Barley can be sweated up to 130° F. See J. R. Dixon, *Journ. Inst. Brewing*, 1912, xviii., 105.



**Cleaning and Grading the Barley.**—The barley is next passed through a rough cleaning machine so as to remove the coarse impurities it contains by means of sieves and blower fans. Then it is sorted out by special "grading" machines into grains of different sizes, which must be steeped separately; for if the grains are of different sizes they will germinate at different rates, and one set of grains will be ready for curing before other sized grains have attained the proper condition. Also, all broken and half corns must be removed, for if such half corns are allowed to get on to the growing floor, they set up mould and create a lot of trouble, often damaging a whole piece of malt.

The Rougher Out may be made either in the form of wire sieves or a rotary wire cylinder enclosed in a wood or iron frame, and having an efficient fan to extract dust and light straws from the machine while in work. An advantage of the machines with sieves is that they are more easy to clean, and the exhausting arrangements are more efficient.

The barley cleaning machine for finishing is very similar in outward appearance to the Rougher Out, but has additional sieves for taking out very thin barley (which is fit only for chicken food), heavy sand, etc. This machine again has a powerful exhausting fan operating over the whole surfaces.

After the barley leaves this machine it passes into half corn separators, which are made from plates of a special metal having indentations (not holes) drilled at regular distances all over their surface. The plates are then rolled into cylindrical form, mounted on a spindle and carried in a wood or iron frame with a slight slope from feed end to delivery end. The cylinders are rotated by means of pulleys and belt; or by bevil gears. The barley is fed into the cylinder, and finds its way into the indentations. The whole

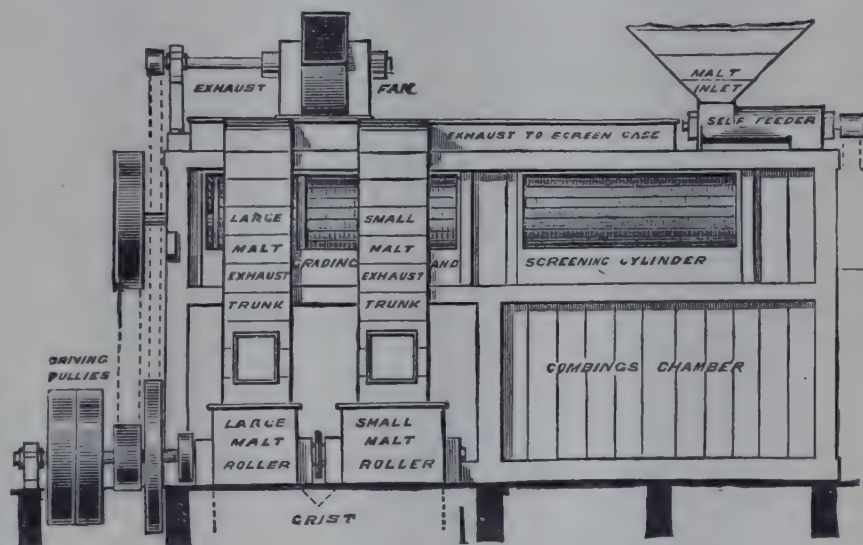


FIG. 100.—Machine for Cleaning and Grading Barley, Malt, and other Grain.  
(Llewellyns & James, Bristol.)

corns project for about a third of their length beyond the surface of the plates, and as the cylinder rotates they come into contact with the edge of a tray mounted on the spindle. Contact with this tray has the effect of knocking the whole corns back into the bottom of the cylinder, while the half corns, not projecting in the same manner, are carried beyond the edge of the tray until compelled by gravity to fall into the tray, which is fitted with a worm carrying the half corns out at the end, the whole corns also being carried by the slope of cylinder and the pressure of incoming barley to the end where they are delivered from the machine by a different exit. The whole corns, which of course comprise the thoroughly cleaned barley, should be put into bins reserved for this purpose either directly over the steeping cisterns or so as to command them easily.

**Dust Control.**—In the case of both Rougher Out and Barley Dresser, it is necessary that means should be employed to effectually deal with the dust from the exhaust fans. The old-fashioned way of doing this was to allow the fan to blow into a chamber called a dust chamber or stive room. This chamber had an outlet for the spent air to escape to the open, while the dust was precipitated on to the floor, from which it was afterwards taken away in sacks. This system had many objections, as frequently a large amount of dust was thrown out on to the roof and found its way to the working floors, which was very bad, owing to the presence of various germs. The better way is to allow the fans to discharge into a dust collector, preferably of the dry type, a very good one being that illus-



trated in Fig. 101 which consists of an upper and lower box, connected together by a number of tubes; the air escaping through the fabric, the dust being retained, and settling down to the lower box where it is caught in a worm and delivered to sacks on the floor beneath. In order that the pores may not become clogged, a cleaning attachment travels continuously up and down the tubes. The apparatus is extremely effective in work.

**Steeping the Barley.**—The cleaned and graded barley is now conveyed to the steeping cisterns, and moistened with water in order to start process of germination.

The cisterns for steeping should be made of cast iron with conical bottom in order to be self-emptying. Spargers should be fitted round the four sides at top and an overflow trough with a grid to retain floating corns on one of the top side plates. A very good adjunct to a steeping cistern is a

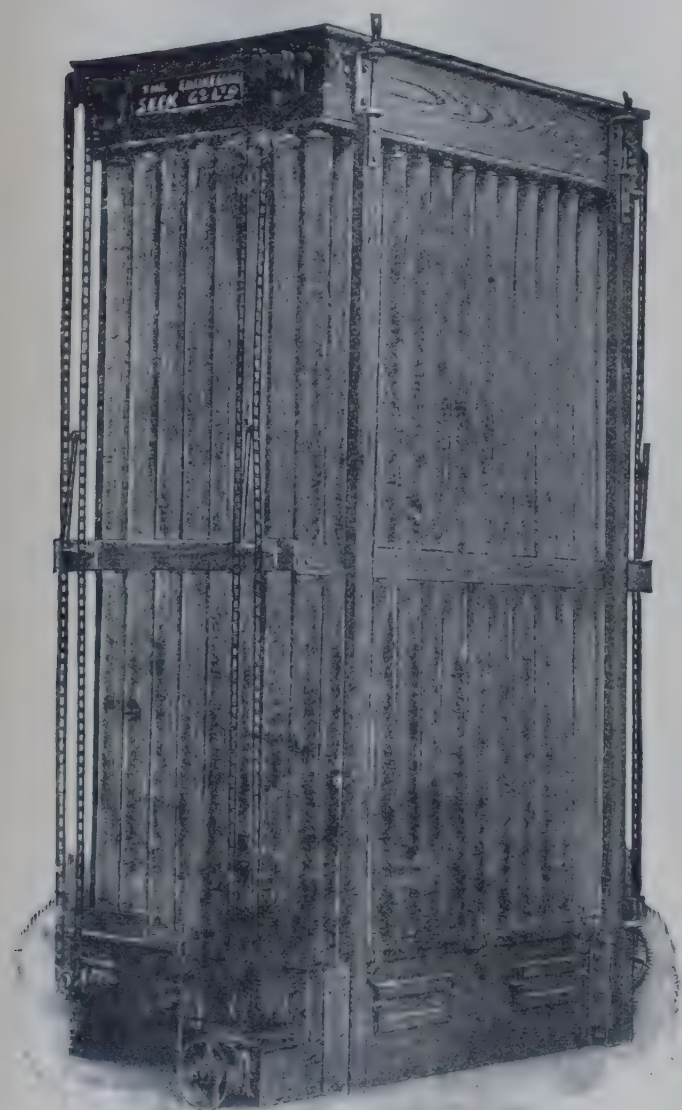


FIG. 101.—Dust Collecting Machine.  
(Seck Engineering Co., London.)



FIG. 102.—German Aerating Cistern for Steeping Barley.  
(Gebrüder Sachsenberg, Rossau in Anhalt, Germany)

system of aeration, an idea originating from Germany. It consists of an air compressor and receiver: the air is forced into the steep through a valve fitted to the water inlet pipe and a certain quantity of air goes in with the water. At varying intervals during steeping, air is let into the cistern, causing the barley to move about or "boil up," thoroughly aerating it and assisting the regular germination, besides, as is claimed, shortening the time for steeping and couching.

The size of steeping cistern can be obtained from the fact that a mixture of barley and water in a cistern occupies 14.15 cub. ft. per quarter. The barley after being in the steep about forty-eight to sixty hours, at a temperature of about 50°-54° F., should have the water drained away by means of the valve fitted at the bottom for that purpose, the grain being prevented from going with the water by means of a slotted or perforated gun-metal grid. This grid is attached to a door covering the bottom of steeping cistern, the door itself being carried on a vertical pin secured to the lower part of cone. This pin forms a hinge allowing the door to be swung round horizontally clear of the opening permitting the grains to fall on to the working floor.



**Growing or Germinating Floors.**—The malt-house usually consists of several floors. The wet grain falling on these from the steeping cistern is levelled down to a depth of 2-3 ft. This is called a **couch**, and the operation is known as **couching**, and is done to cause a sufficiently high temperature to make the grain commence to germinate properly. When the barley begins to sprout or grow, small hair-like rootlets are produced, and heat is generated during growth; the temperature must not be allowed to increase more than a certain amount (60° F.). Hence, when growth has started the couch is broken down and spread over the floor to a depth of about 3-4 in. This is called a piece of malt, and the depth must be varied according to the rate of growth and the varying temperature in the malt-house, as it is obvious that if the thickness is too great and the temperature high, forcing will result; while, on the other hand, if the thickness is not sufficient and the temperature low, then the growth will be retarded, and indeed often stopped altogether.

Moreover, since for uniform growth the malt requires air, it is necessary to aerate the growing barley (which is now known as "**green malt**"). This is



FIG. 103.—Malt House (Malt Growing on Floor), Guinness's Brewery, Dublin.

done by turning the malt with shovels about twice a day. During the turning the green malt is thrown through the air in a thin stream, whereby it is aerated and cooled. It is often ploughed by means of a hand plough which aerates without the need of the heavy labour of completely turning the piece. During the turning process the malt is gradually worked along the floor, being sprinkled when necessary to assist growth, until it arrives at the kiln end of the malting, and it is then considered sufficiently grown. This usually occupies from nine to thirteen days, depending upon the character of the barley, and the quality and character of malt it is required to produce.

The chemical changes which have taken place in the barley up to this stage is the secretion of the enzymes **cytase**, **diastase**, and **peptase**. The **cytase** dissolves the cell-walls within the endosperm, enabling the **diastase** to attack the starch, converting it, according to the requirements of the growing plantlet, into diffusible and readily assimilable sugar; at the same time the **peptase** attacks the albumoids (proteids), converting them into soluble **peptones**, **amides** (such as glutamine and asparagine), and amido-acids (*e.g.*, tyrosine and leucine).

The formation of these soluble nitrogenous bodies at this stage are of great importance for the nourishment of the embryo and, later, the growing yeast.



If the growth of the germinated malt continues beyond the limit now attained, a serious loss of starch and sugar will result. The further growth of the barley is therefore checked by—

**Withering.**—That is, the rootlets are allowed to fade and wither by withholding any further outside supply of moisture to the grain. The withering stage occupies about twenty-four hours, and the malt is then loaded on to the kiln. Moisture at loading-on should be less than 40 per cent. This loading used to be done by hoisting the green malt in sheets or baskets, and indeed is done so at the present time in a good many of the older malt-houses. The modern system is, however, to employ elevators for the purpose.

**Kilning or Drying.**—The malt remains on the kiln for about three to four days, drying and curing, two days being taken up for drying and two for curing. During the time the malt is on the kiln for this purpose it is turned frequently so as to allow the heat from the furnace to come into contact evenly with the whole of the malt.

The kiln usually has only one floor made of wire or tiles, and heated by means of a closed furnace below. The roof is constructed in the form of a pyramid, having outlet at the top, with adjustable doors for carrying off the vapours. In some modern kilns suction fans are placed in the outlets to accelerate the drying. The green malt is evenly spread upon the kiln floor about 12-18 in. deep and frequently turned during the drying and curing process. In Scot-

land the kilns usually have two floors made of wire, placed one above the other, and heated by a furnace or open fire from below. The green malt is evenly spread upon the upper kiln floor about 18 in. deep. It remains here twenty-four hours, and is then only partially dried. It is then dropped upon the lower floor, again

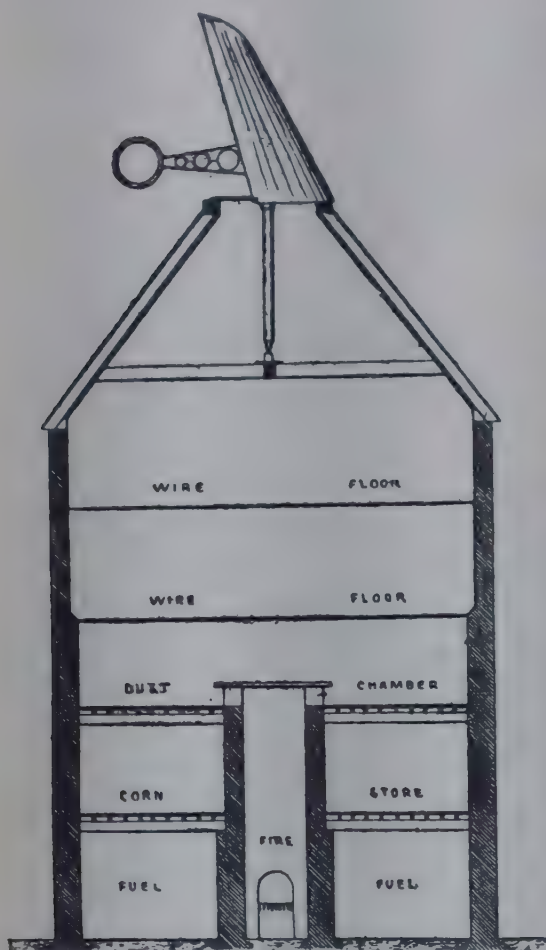


FIG. 104.—Scottish Two-floor Malt Kiln. (Messrs Bryan, Corcoran Ltd., London.)

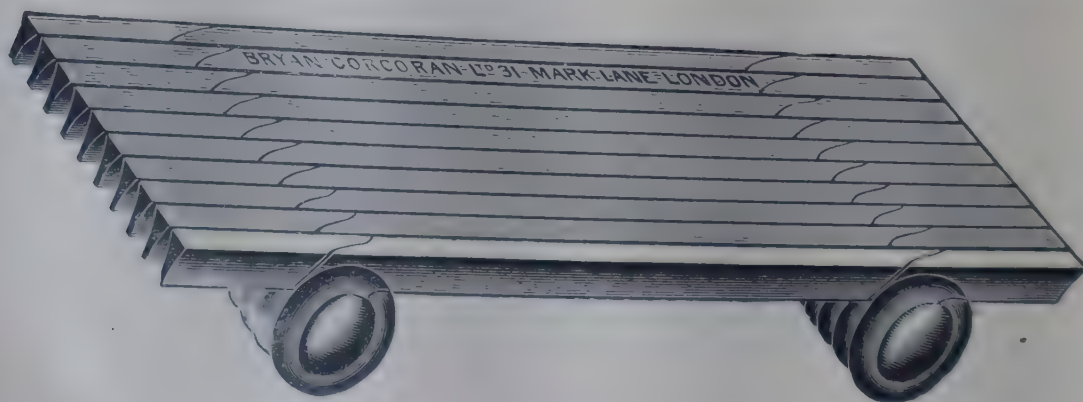


FIG. 105.—Patent Steel Flooring for Malt Kilns.

spread evenly, and subjected to a higher temperature until the desired degree of dryness is obtained.

The heat is obtained by means of shaft furnaces as shown, and good anthracite coal is most generally employed—coke being unsatisfactory owing to the fumes depositing arsenic on the malt.



This latter objection is due to the practice in English malting of allowing the products of combustion to come into direct contact with the drying malt.

For the drying stage the temperature usually commences at about 80° F., rising gradually to 120° F., while for curing, the temperature is raised from the latter figure to 160° or up to 200° F. for a pale malt, and higher than this where high coloured or porter malts are required.

The turning of the malt on the kiln in modern maltings is done by means of an Automatic Kiln Turner, which ensures that the whole of the malt is thoroughly turned, obviating the risk of getting vitrified or unevenly coloured malts which often happens where the turning is done badly by hand.

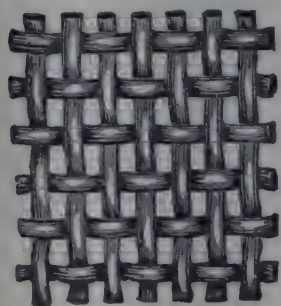


FIG. 106.—Wire Flooring of Malt Kiln.

The malt being completely dried and cured is allowed to cool, and is then emptied into the bins under the hot air chamber forming the warm malt store.

The emptying is done by means of a number of steel pipes led from the kiln floor to the bins, the malt being shovelled into heaps over each pipe, from which the cover is removed, and while a large amount will run down by gravity the remainder is swept into the pipes by the maltster. From these bins the malt is either lifted up by means of an elevator and distributed by a band conveyor to the main malt stores, or it is first screened and then put into stores. Where the second method is adopted it is often usual to screen again before sending out the malt—although this is not absolutely necessary provided a thoroughly good malt screen is first employed.

The choice of these two methods of dealing with the malt lies with the individual maltster, opinion being very divided as to whether it is better to store the malt with the culms on or not.

The malt stored in suitable bins may be preserved without injury for twelve months or longer. Malt will keep almost indefinitely if stored with not more than 3% moisture.

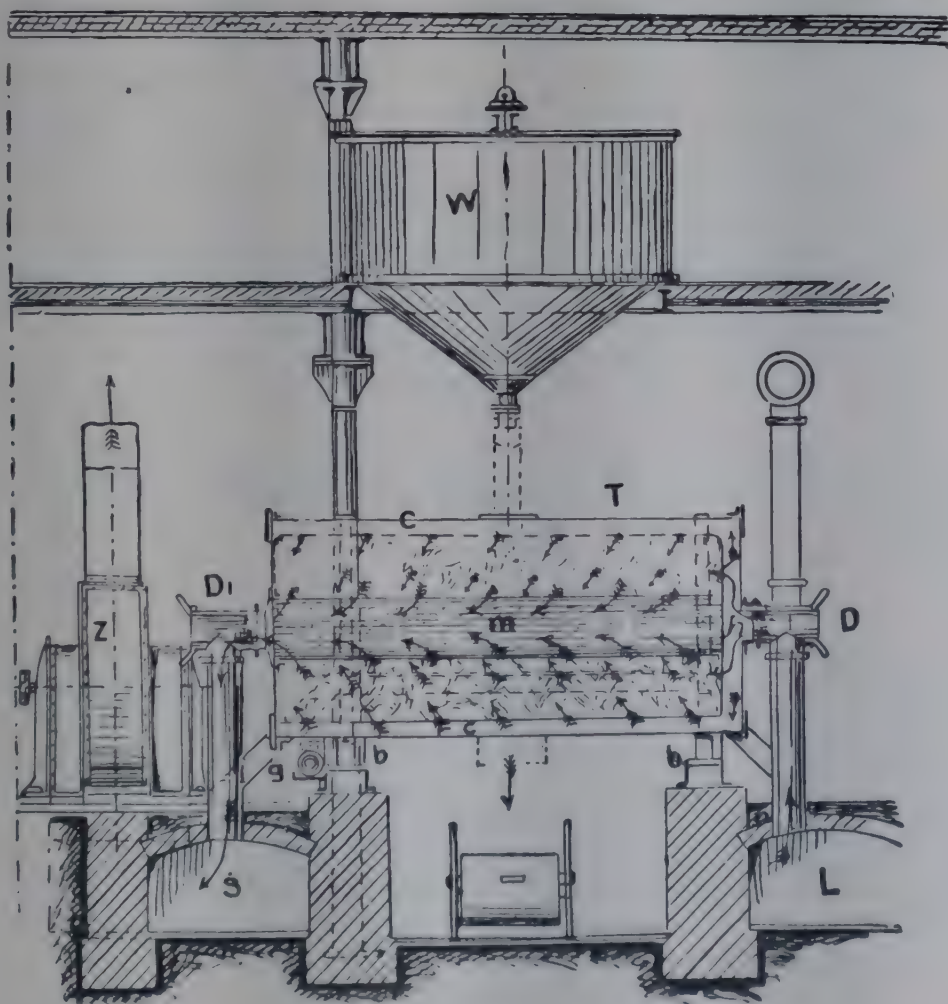


FIG. 107.—Galland's Pneumatic Malting Drums.



## PNEUMATIC MALTING

The foregoing is the general system of malting as used in England. There is, however, another system used to some extent in England known as pneumatic malting. In this process the grain, after being steeped in the same way as for floor malting, is put into revolving germinating drums (Figs. 107, 108).

These drums are only partly filled with grain. They are constructed with an outer shell of steel plate and an inner cylinder of perforated metal. Running through the centre of the cylinder throughout its length is a tube of similar perforated metal. Each end of the cylinder is connected by means of pipes to air ducts built below the level of cylinders. One of these ducts, L, is connected at one end to a tower through which the air is compelled to pass, and in passing, this air is purified and moistened, as well as heated by a steam jet when necessary.

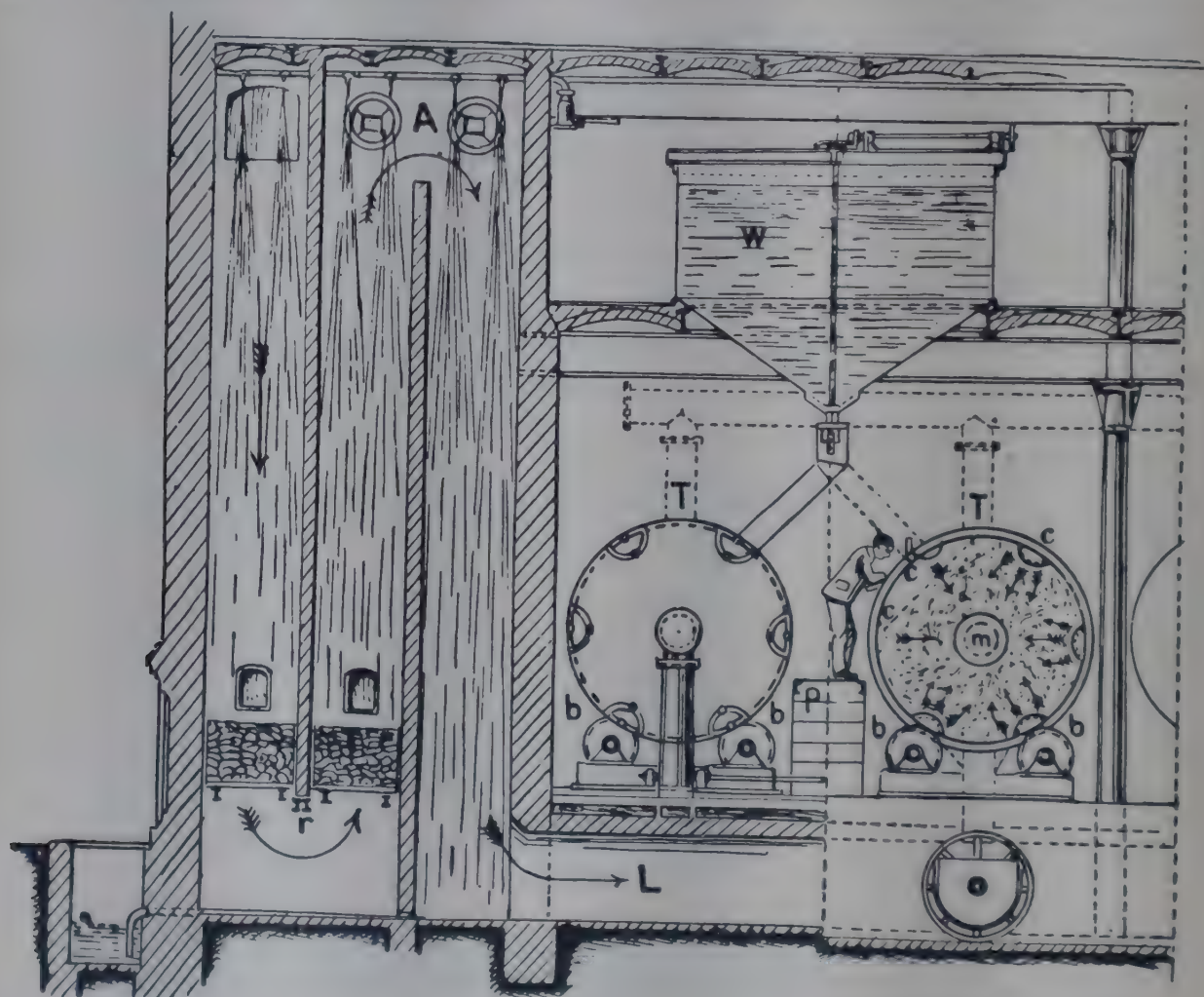


FIG. 108.—Galland's Pneumatic Malting Drums.

The drum is revolved very slowly by means of a worm gear, the weight of drum being carried by rollers mounted on spindles carried in heavy bearings.

When the cylinder is in work, the fan induces a current of air from the air tower through the duct L and thence by means of the pipes to the cylinder, through the grain, into the perforated tube, down the pipe at back of cylinder, and thence by the duct S is sucked into the fan and discharged into the open air. Provision is also made for delivering heated dry air into the cylinders. The drying and curing means of a drum working substantially in the same manner as the germinating drums.

This system of malting has advantages in economy of space and in saving of labour, but it is regarded as being very expensive in first cost and in subsequent upkeep. There are a number of



plants at work in Great Britain, although maltsters generally do not view the results from them very favourably.

Another system of malting which, like the former, is of German origin, is the Plischke system, a patent device which consists of a number of moving wire beds. The grain is delivered from the steeping tank on to the top bed and this moves over end rollers very slowly. The growing grain is discharged from the top to the next bed and then to the next, and so on till when it is finally discharged from the bottom bed the process of germination is completed and the "green malt" is ready to load on to the kiln.

Another system in vogue in Germany is that in which the malt is grown, *i.e.*, germinated on floors in the same way as in England, but the turning and ploughing of the growing grain is done by a specially constructed and patented machine. In the matter of kilns the German system is generally that the hot gases do not come into direct contact with the malt during the curing process, but they are conducted through pipes running under the kiln floors, which are made of wire, and the air passing over these pipes becomes heated and is drawn through the wire floor and consequently through the malt, thus drying and curing it.

**Storing and Conveying Barley and Malt.**—In the malt-house described we assume that the barley will be brought in trucks or carts, and stored in bulk, that is in bins, and for this purpose bins with self-emptying conical bottoms are used.

It is usual to allow 10 cub. ft. per quarter for **barley**, and 12 cub. ft. per quarter for **malt**, when storing in bulk in bins.

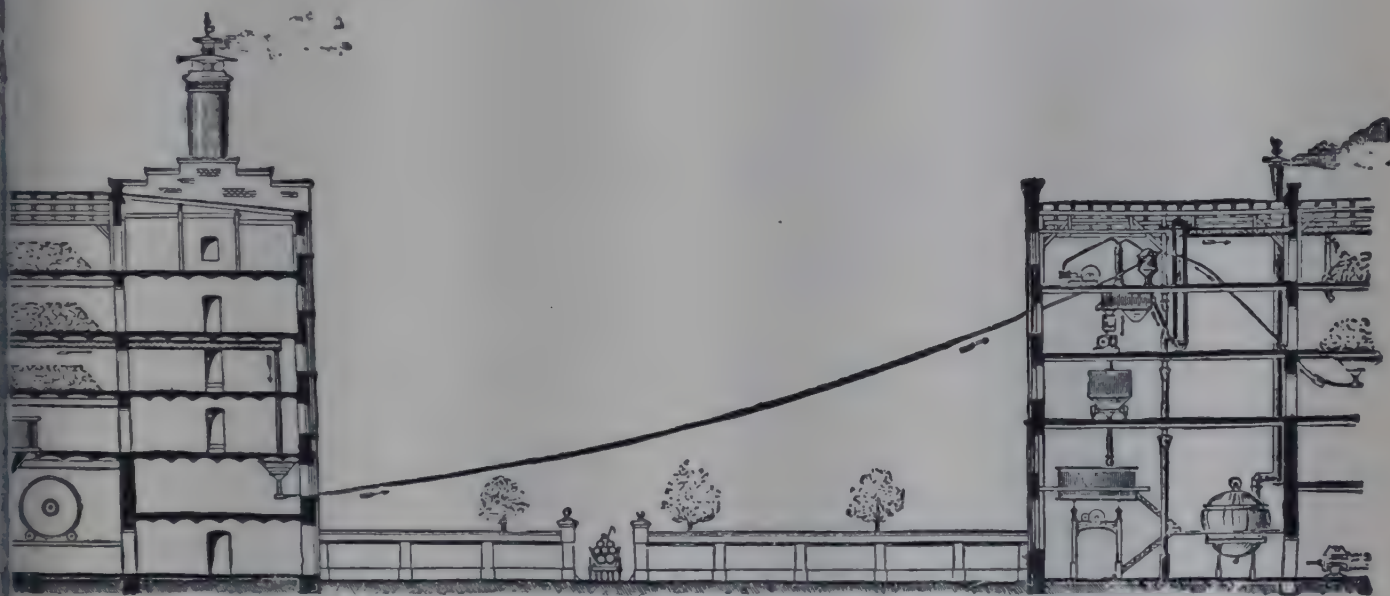


FIG. 109.—Pneumatic Transport of Malt from Malt House to Brewery.  
(Seck Engineering Co., London.)

The method of filling the bins has usually been done by means of a sack hoist, but for various reasons this is not advocated, an elevator, or, as it is sometimes called, a Jacob's ladder, being much preferable. This should command a band conveyor in roof with a movable throw-off carriage, delivering into the barley stores by means of pipes, and if this band is made to reverse so as to run in either direction, the roof can be made to serve as a barley store, so as to facilitate buying in large quantities at the commencement of the season. The reason for making the band conveyor reversible is that by means of one or two small intermediate elevators, the barley stored in the roof can be brought back over the cleaning machinery or steeping cistern for steeping.

While elevators and band conveyors are very largely used for conveying and transporting grain, there are a great number of occasions when it is impossible to make use of these appliances.

Where such conditions arise, the system of transporting grain by means of air suction is extremely useful. It can be used for connecting buildings up to 300 or 400 yds. apart from each other, and of varying elevation, without the need of any bridge, such as would be the case with band conveyors, while the absence of large elevator trunks going through floors is a great safeguard against fire. The tubes vary from about 3 in. to 6 or 7 in. diameter, and a great feature in their use is that corners can be readily negotiated, and rigid straight lines need not be adhered to.

The illustration shows very clearly one of the uses that the Pneumatic Transport can be put to.

**Composition and Yield of Malt.**—In general, 100 parts of air-dried barley yield 70-75 parts of cured malt. In the case of very nitrogenous barleys the loss is greater than this. During the storing, the malt absorbs some per cent. of moisture.

100 parts of barley, containing 86 per cent. dry substance, lose :—

In steeping	-	-	-	-	1.3 per cent.
During germination by the evolution of gases like CO <sub>2</sub>	-	-	-	-	5.1 "
Other losses during germination	-	-	-	-	4.0 "
Total loss	-	-	-	-	<u>10.4 per cent.</u>

J. S. Baker (Allan's "Commercial Analysis," vol. i., p. 133, 4th ed.), gives the following figures to illustrate the difference between barley and malt (English) :—

	Moisture.	Proteins.	Fat.	Sugar and Gum.	Starch.	Fibre.	Ash.
Barley - -	15	10	2	11	55	5	2
Malt - -	2	11	0	16	63	6	2

## ANALYSIS OF MALT.

### LITERATURE.

**JULIAN S. BAKER.**—Allan's "Commercial Analysis," 4th Ed., vol. i., p. 134, gives an excellent account.

Reports of the Malt Analysis Committee, 1905.

" " " " on "Coloured Malts and Caramel," 1910. (Price 7d.). Institute of Brewing, Brewers Hall, Addle Street, London, E.C.

**G. CECIL JONES.**—"Standardisation of Malt Analysis." (*Journ. Instit. Brew.*, 1905).

" " " " "Diastatic Power by Lintner's Method." (*Ibid.*, 1907).

**H. T. BROWN.**—*Journ. Instit. Brew.*, 1916, xxii, 267.

**A. FERNBACH.**—*Journ. Instit. Brew.*, 1916, xxii., 370.

**H. HERON and J. M. HERON,** *Journ. Instit. Brew.*, 1914, xx., 465; 1902, viii., 666.

**A. R. LING.**—*Journ. Instit. Brew.*, 1900, vi., 355; 1902, viii, 441.

See also numerous other papers in the *Journ. Instit. Brew.* within recent years.

The brewing value of a sample of malt depends upon (1) amount of soluble extract it yields to water and nature of same; (2) its diastatic capacity.

*To Sample.*—Draw from one sack in ten at a depth of at least 6 in., put into small bin, mix, and collect samples in clean screw-stoppered beer bottles.

For analysis, grind in a "Seck Laboratory Mill" set at 25°, and grind separately for each determination.

**Extract Determination.**—Mash 50 g. in a 500 glass beaker with 360 c.c. of distilled water, previously heated to 68° C. (154°-155° F.). Cover with clock glass and place in water bath to keep at 66° C. (150° F.) for fifty-five minutes, stirring at intervals of ten minutes. Then heat to 70° C. (158° F.) for five minutes, and wash into a flash graduated to 515 c.c. (15 c.c. = allowance for volume 50 g. malt). Cool to 15.5° C. (60° F.), make up to mark with distilled water, and filter through a large-ribbed filter paper. Take sp. gr. at 15.5° C. (60° F.), taking water at 60° F. = 1,000.

The excess sp. gr. over water (= 1000) multiplied by 3.36 gives extract in brewers' pounds per standard quarter of malt.

**Colour of Wort.**—Place immediately clear filtered wort in 1-in. cell of the Lovibond tintometer, and record tint in colour units of the series of "52" glasses. Avoid direct sunlight, and



reverse glasses and cell to be certain the field is equally illuminated. (See J. L. Baker and H. F. E. Hulton, *Journ. Instit. Brew.*, 1906, 12, 302; 1907, 13, 26; Lovibond, *ibid.*, 1908, 14, 2.)

**Moisture.**—5 g. of ground malt are heated five hours in boiling water oven in a copper dish 5 cm. diameter and 1.25 cm. depth. Loss of weight represents moisture.

**Diastatic Activity** (Lintner value).—The diastase acts on the starch and produces the sugar maltose. The amount of maltose produced may be taken as proportional to the diastatic activity of the solution, provided that the production of the maltose does not exceed 45 per cent. of the starch. (See Kjeldahl, "Compt. rend. des travaux du laboratoire de Carlsberg," 1879, i., 109; also A. R. Ling, *Journ. Fed. Instit. Brew.*, 1896, 2, 335.)

The water used should be redistilled, with the addition of a little potassium permanganate and sodium hydroxide. The water must be free from ammonium salts and quite neutral.

The soluble starch used is prepared by digesting 500 g. purified potato starch for seven days with 1,000 c.c., of dilute HCl, sp. gr. 1.037, washing until free from acid, first by decantation with tap water, and later with distilled water in a Buchner funnel. Dry quickly at 110° F. (43.5° F.), triturate in mortar, and pass through fine hair sieve.

The soluble starch solution used contains 2 g. starch to 100 c.c. water. Add the starch to the boiling water, and cool to 70° F. for use. It must be neutral to litmus, only very slightly reduce Fehling's solution, and be mobile (not gelatinous).

**Process of Determination of Diastatic Activity.**—Extract 25 g. of ground malt for three hours at 70° F. Filter. Neglect first 100 c.c., add 3 c.c. of clear extract to 100 c.c. of the 2 per cent. solution of soluble starch in a 200 c.c. flask at 70° F. Keep for one hour at 70° F., then add 10 c.c. N/10 alkali to stop further diastatic activity, cool to 60° F., and make up to 200 c.c. with distilled water. Then titrate against 5 c.c. portions of Fehling's solution as follows:—

Place 5 c.c. Fehling's solution in 150 c.c. boiling flask, heat to boiling, and add the converted starch solution from a burette in quantities of about 5 c.c. at a time, shaking the mixture after each addition over the naked flame, and boiling until reduction of the Fehling solution is complete, which is ascertained by withdrawing a drop of the liquid by means of a glass rod, and bringing it at once into contact with a drop of ferrous thiocyanate solution on a porcelain slab.

If  $A'$  represents the diastatic activity,  $x$  the number of cubic centimetres of malt extract contained in 100 c.c. of the diluted starch conversion solution, and  $y$  is the number of cubic centimeters of same liquid required to reduce 5 c.c. of the Fehling solution, then

$$A' = \frac{1000}{xy}.$$

When the malt has a diastatic activity over 50 Lintner, use 2 c.c. of malt extract to 100 c.c. of 2 per cent starch extract.

**Cold Water Extract.**—Digest for three hours at 70° F. 25 g. ground malt with 250 c.c. of distilled water containing 20 c.c. N/10 ammonium hydroxide. Stir at intervals. Filter. Take sp. gr. at 60° F. (water=1000). Then cold water extract is given by excess sp. gr. over 1,000 (corrected for sp. gr. of the ammonia solution) divided by 0.386. English malts average 18 per cent. cold extract.

**Acidity of Malt.**—Digest 50 g. ground malt with 300 c.c. of distilled water at 60° F. for three hours, and titrate with N/10 ammonium hydroxide, using litmus as indicator.

Calculate acidity as *lactic acid* (really due to acid phosphates).

**Nitrogen.**—Determine by Kjeldahl's method. Per cent. N  $\times$  6.25 gives nitrogenous matter.

**Saccharification Test.**—Mix 10 g. ground malt with 100 c.c. water at 154° F., and keep at 151° F. stirring mash. In fifteen minutes withdraw 5 c.c. of mash, cool, and test in starch by iodine. Repeat every five minutes until the solution no longer reacts for starch.

This gives the time required for the complete saccharification of a malt mash.

**Sinker Test.**—Throw 500 malt corns into cold water. Remove floating corns. Vitreous corns, etc., will sink to bottom, and can be counted.

**Growth.**—200 malt corns are sorted into the following six groups according to development of acrospire: 0 to  $\frac{1}{4}$ ;  $\frac{1}{4}$  to  $\frac{1}{2}$ ;  $\frac{1}{2}$  to  $\frac{3}{4}$ ;  $\frac{3}{4}$  to 1; overgrown corns; damaged corns.

English malt should contain 80-100 per cent. corns from  $\frac{3}{4}$  to fully grown.

**Test also for Arsenic.**

State results, thus:—

Extract per standard quarter, brewer's pounds.

Moisture, per cent.

Diastatic activity (Lintner value).

Tint (10 per cent. wort, 1 in. cell, "52" series Lovibond).

Cold water extract per cent.

## BREWING

**Theory of Brewing.**—The malt contains, as we have already seen, a considerable amount of starch and its degradation products. It also contains the enzyme diastase in considerable amounts. The malt is crushed and mixed with hot water (160°-168° F.) in a mashing vat. The diastase now acts powerfully upon the starch, converting it into sugars.

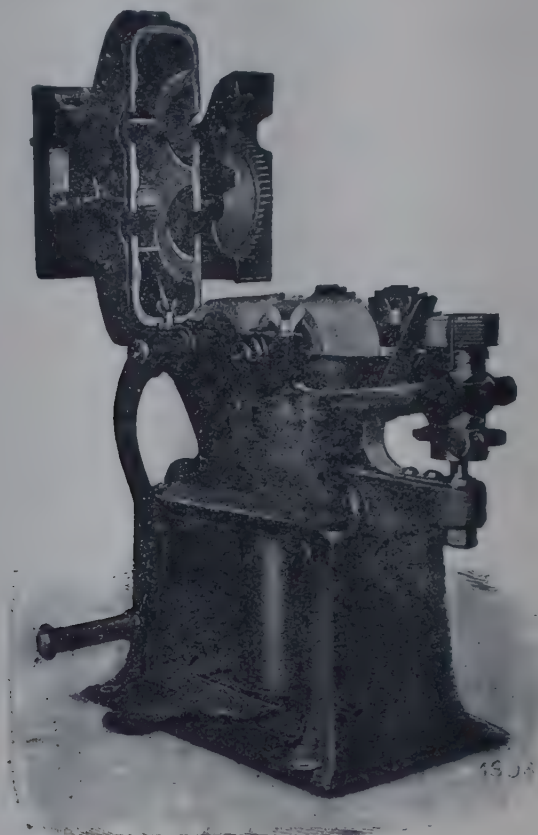
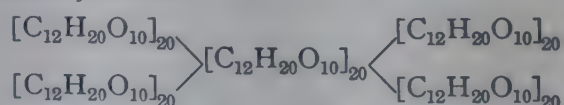
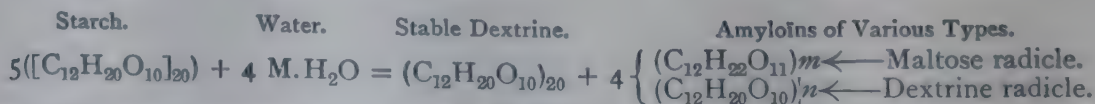


FIG. 110.—“Seck” Laboratory Mill.  
(Seck Engineering Co., London.)

The diastatic degradation of starch is no simple change. According to Brown and Morris the starch molecule consists of five amylin groups, each of formula  $[C_{12}H_{20}O_{10}]_{20}$ , four radicles being grouped centrally round the fifth, thus:—



Diastase splits up this complex molecule, hydrolysing it into four groups of amyloins, while the central amylin group remains unchanged (and not being attacked by alcohol-producing enzymes, is left unchanged throughout the whole course of brewing operations), forming what is known as **stable dextrine**, according to the equation:—



The amyloins are compounds of maltose and dextrine, and exhibit the properties both of maltose and of dextrine.

As the process of hydrolysis proceeds the amyloins pass into lower degradation products which are richer in maltose, the final product of transformation being **maltose**. Several amyloins have been isolated, *e.g.*,  $(C_{12}H_{20}O_{10})_6 \cdot (C_{12}H_{22}O_{11})$  (amylo-dextrine) and  $(C_{12}H_{20}O_{10})_2 \cdot (C_{12}H_{22}O_{11})$  (malto-dextrine).

The amyloins are not split up in the primary fermentation; in the secondary fermentation they are converted, more or less rapidly according to their type, into maltose. They are of two types, “high” and “low.” A beer of a stable character must contain a considerable proportion of high-type amyloins (which are the first product of the action of diastase on starch), and consequently is produced by restricting the action of diastase in the mash-tub. A beer which is to “condition” rapidly must contain a sufficient amount of low-type malto-dextrine (which are later products of the action of diastase on starch).



The type of malto-dextrine ultimately produced from the starch in the malt can be regulated both in the malt-kiln and in the mash-tub. Higher types are produced by *low kiln* and *high mashing* temperatures, whereas lower types are produced by *high kiln* and *low mashing* heats.

It is therefore possible to regulate on scientific lines both the quantity and the type of amyloins which are suitable for a particular beer.

The hydrolysis of the starch by the **diastase** proceeds best between  $40^{\circ}$ - $60^{\circ}$  C., but the temperature is often raised to  $70^{\circ}$  because the starch should be gelatinised, the attack being then more rapid. The starch of the malt dissolves much more easily than that of the raw grain. The dextrines produced,  $(C_{12}H_{20}O_{10})_n \cdot H_2O$ , are amorphous, reduce Fehling's solution, and are strongly dextro-rotatory. As the molecule breaks up under the action of the diastase the dextro-rotary power diminishes while the power of reducing Fehling's solution increases.

Only the low-grade dextrines are fermentable with yeast.

The following table shows the rotary and copper-reducing power of some of the products of the break up of the starch molecule :—

	Specific Rotation [ $\alpha$ ] <sub>D</sub> .	Copper-Reducing Power (Maltose = 100).
Soluble starch, $(C_{12}H_{20}O_{10})_n$ - - - -	+ 198°	0
Amylo-dextrine, $(C_{12}H_{20}O_{10})_7 \cdot H_2O$ - - -	+ 187°	9
Malto-dextrine $\alpha$ , $(C_{12}H_{20}O_{10})_3 \cdot H_2O$ - - -	+ 180°	33
Malto-dextrine $\gamma$ - - - - -	+ 170°	60
Maltose, $(C_{12}H_{22}O_{11})$ - - - - -	+ 137°	100

The **Maltose**,  $C_{12}H_{22}O_{11} + H_2O$ , is easily soluble in water, crystalline, tasting but slightly sweet. It hydrolyses with acids into 2 molecules of dextrose and gives with **phenyl hydrazine** a difficultly soluble dextro-rotary osazone,  $C_{24}H_{32}N_4O_9$  (see pp. 166, 167, Glucose).

Under favourable conditions over 80 per cent. of starch can be converted into dextrose by diastase, the other 20 per cent. remaining as dextrine in the liquor. After the destruction of the maltose by the yeast, this dextrine is slowly hydrolysed to maltose.

As will be seen in the next chapter it is the object of the *distiller* to convert *all* his starch into **maltose**, but the brewer, on the other hand, intentionally leads the mashing process in such a manner that a large amount of unfermented dextrine remains in the beer and as "extract" forms the nutritious part of the beer. Hence in brewing matters are arranged so that only about 60 per cent. of the starch is transformed into fermentable carbohydrates.

In order to obtain a dark beer and produce a pronounced malt flavour **caramel** and black malt (*i.e.*, malt browned by heating to a considerable temperature in rotating drums) are added in small amounts mixed with other materials. Malt substitutes, raw grain, and brewing sugars are also added at this stage: (1) for producing very stable beers, since they contain little albumen; (2) for producing paler beers than could be produced with malt alone; (3) for reducing the cost of production. Among such products may be mentioned raw grain, rice, corn grits, corn meal, maize flakes, brewing sugars, etc. Flakes are produced by steaming corn grits and passing them through hot steel rollers; this makes them dissolve better during mashing. Raw grain, corn grits, rice, etc., require previous cooking, whereas flakes are added directly to the wort in the kettle. Brewing sugars are used for producing lager beers, English ale, stout, etc.

The mashing takes about three hours. The hops are added to the boiling wort for the purpose of imparting (1) **tannin**, which forms insoluble compounds with albuminoids, and thus causes them to coagulate out; (2) **hop oil**, which gives the beer its hop aroma; (3) **hop resin**, which imparts to the beer a bitter taste and also acts as a preservative.

While adding the hops the wort is thoroughly boiled, the best hops being added last, so that the volatile hop oil may not be driven off. The boiling sterilises the wort and coagulates the albuminoids, which separate in flakes.

The wort is then run off, cooled to a suitable temperature in a refrigerator (56°-60° F. for English top-fermenting beer), and the yeast is added to the wort in the fermenting tanks. The yeast rapidly develops, and converts the sugars into alcohol and carbon dioxide by what is called "**primary fermentation**," thus converting the wort into beer. The yeast is then separated and this beer stored in tuns, where it ripens, undergoing **secondary fermentation** ("*after*" fermentation).

### Waters for Brewing Purposes

**Waters adapted for producing pale ales** contain calcium sulphate in fairly large quantity. Thus the **Burton waters**, which are extremely well adapted for this purpose, have the following composition :—

	Grains per gallon.		Grains per gallon.
Calcium sulphate - - -	77.9	Sodium chloride - - -	3.9
Magnesium carbonate - - -	21.3	Sodium nitrate - - -	2.0
Sodium sulphate - - -	10.2	Potassium sulphate - - -	1.6
Calcium carbonate - - -	7.62	Silica and alumina - - -	0.98

The best brewing effect is obtained from 40-50 grains of  $\text{CaSO}_4$  per gallon.

**Waters adapted for producing black beers** must be soft, containing, however, fairly large amounts of calcium and magnesium carbonates. Since these latter substances are almost entirely precipitated by boiling, the water as actually used in the brewery contains only 2-3 grains of solid matter per gallon. London and Dublin well waters are well suited for beers of this type. An analysis of a Dublin well water gave :—

	Grains per gallon.		Grains per gallon.
Calcium carbonate - - -	14.2	Magnesium carbonate - - -	0.90
Calcium sulphate - - -	4.4	Silica - - -	0.26
Sodium chloride - - -	1.83	Iron oxide and alumina - - -	0.24

**Waters adapted for producing mild ales** must contain a large amount of chlorides and little calcium sulphate. The following is a typical analysis :—

	Grains per gallon.		Grains per gallon.
Sodium chloride - - -	35.1	Magnesium carbonate - - -	4.0
Calcium chloride - - -	3.9	Iron oxide and alumina - - -	0.24
Calcium carbonate - - -	16.4	Silica - - -	0.22
Calcium sulphate - - -	6.2		

No single water possesses the qualifications necessary for producing every class of beer. To render a water suitable for producing a given type of beer it is necessary to analyse it accurately and then add to it the proper amount of calcium sulphate, magnesium sulphate, calcium chloride, etc., to bring it up to the standard conditions. If a water contains too much calcium sulphate it is usual to *dilute* the water with a soft one so as to reduce the percentage of  $\text{CaSO}_4$  to the proper amount. In some cases precipitation by  $\text{Na}_2\text{CO}_3$  is resorted to for removing the  $\text{CaSO}_4$ . The addition of  $\text{Na}_2\text{CO}_3$ , followed by  $\text{CaCl}_2$ , is resorted to for getting rid of excess of iron.



# THE PRACTICE OF BREWING AS GENERALLY ADOPTED IN ENGLAND

## General Arrangement of the Brewery

In deciding upon a site for a brewery a place must be chosen having a natural supply of good water to draw from, independent of town supply, as the requirements in this respect are very large. The character of beer is governed to a large extent by the quality of the water used in its production. In cases where the water is specially suitable for brewing, large and important brewing centres have been formed. Thus the hard water of Burton-on-Trent has gained for this town a world-wide reputation for pale ales, whilst the softer London and Dublin waters have brought the stouts produced in these centres into equal prominence. As, however, science is now capable of treating water so as to imitate the conditions required, the choice of site is very largely governed by the local demand. The site having been selected and the size and output of brewery having been determined, the general working arrangement of the necessary plant has to be decided upon, and, needless to say, the arrangement should be such as to minimise labour and consumption of power as much as possible.

There are two systems of constructing breweries generally in use, known as the tower and horizontal systems, both having their recommendations. The tower system is worked entirely by gravity, that is to say that the process of manufacture involves treatment floor by floor, descending by stages until the finished beer is ultimately dealt with on the ground floor.

The horizontal system, while it involves a large area, is one enabling the manufacture to be conducted at a low level, very often a great advantage, the process being to erect pumps, elevators, etc., for conducting the material during the stages of treatment from vessel to vessel. Often the system adopted is a combination of the two types of breweries having a minimum of pumping, while at the same time keeping the height of building within reasonable limits.

As a rule the water (or as it is technically known, liquor) is pumped from the source of supply direct into the cold liquor tank at the top of building. From this tank it is drawn by gravity for the purpose of boiling, cooling, and cleaning. The heating of water in the hot liquor tank is performed by steam coils which raise the temperature of the liquor to the desired number of degrees.

The principal ingredients used in brewing consist of malt and hops, although in some cases varying proportions of maize (flaked or in grits), invert sugar, etc., are used, together or separately, these materials in their chemical composition being very similar to malt. For the purpose, however, of this article, we assume that the brewery is one in which malt and hops are used. The malt, the manufacture of which was described in the preceding pages, is brought into the brewery usually in sacks and hoisted to a malt store over the screening and grinding room.

Where the maltings or malt stores are adjacent to the brewery, a great advantage in saving of labour and time and prevention of slackness in malt can be attained by the use of the system of pneumatic transport, introduced into this country by the Seck Engineering Co. Ltd. (see p. 263). In this case the rather dangerous method of hoisting the malt is done away with, and the malt is brought instead from the maltings or stores through tubes by means of air suction, quite free from floating dust.

The malt is then shot from the malt store into a malt hopper which preferably is large enough to contain sufficient for a brew.

The hopper commands the malt screen, which is a machine having revolving wire or perforated cylinders for removing large substances, heavy dirt and culms,



and should be fitted with a polisher to remove any deleterious substances adhering to the skin of the malt (see p. 257).

The clean malt as it leaves the screen is lifted by a short elevator to the malt grinding mill.

This question of grinding has not always received the attention it really merited, and it is only of late years that a really scientific preparation of the grist has been made possible by the adoption of the principle of the Seck Patent Malt Mill. The malt, as it enters this mill, is distributed by means of a very ingenious feed roll, ensuring an accurate and even stream of malt right across the crushing rolls. The mill is constructed with two pairs of rolls, one above the other, and having a sieving device between. The malt is only lightly crushed by the first pair of rolls, and the resulting ground material, which is called grist, falls on to the sieve. This sieve has a reciprocating motion and has the effect of separating the granular grits of the malt kernel, which are sufficiently reduced for brewing purposes, from the husks. These grits pass through the sieve and receive no further treatment, while the husks with any hard steely ends or large coarse grits adhering, pass over the sieve and so to the lower pair of rolls where they are recrushed, the rolls being set closer together

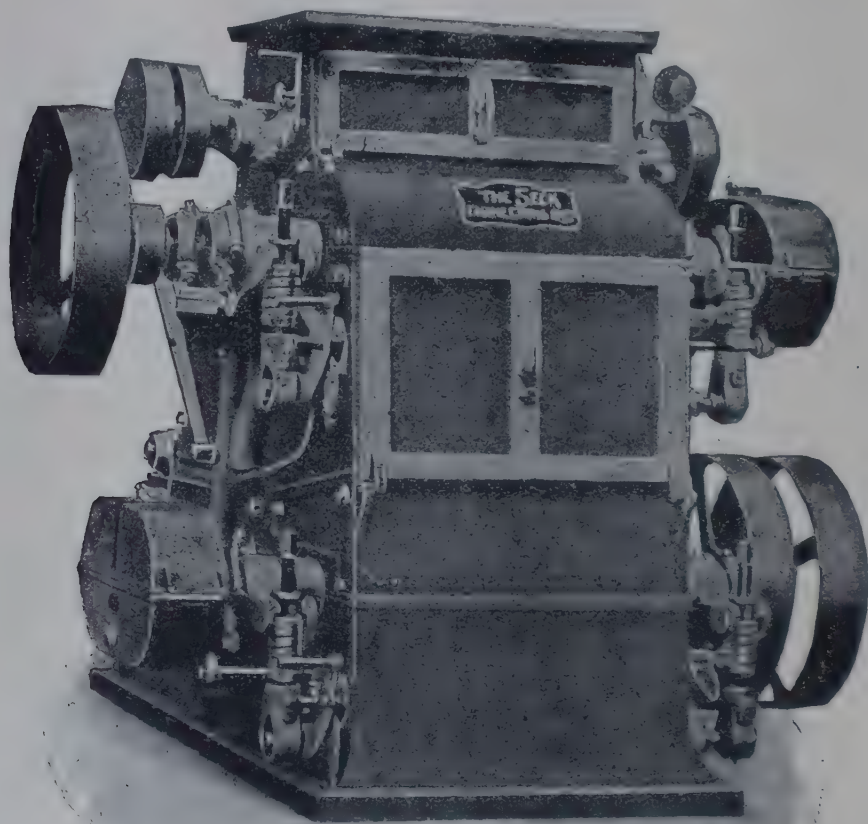


FIG. 111.—Seck Patent Malt Mill. (Seck Engineering Co., London.)

for this purpose. This system of grinding ensures the maximum extract being obtained from the malt, and at the same time gives large flaky husks so essential to a proper filtration or drainage in the mash-tun (see Figs. 111-113).

**Mashing.**—The grinding is usually performed a few hours before mashing, and the grist case should be protected from the effects of damp, as the grist readily absorbs any moisture, and this has a very detrimental effect on the resulting extract, and also on the quality of the finished product. At the bottom of the grist case is fitted a *Steel's* mashing machine (Figs. 114, 115).

This consists of a cylinder having a spindle running through from end to end, and on this spindle are mounted forks and blades placed at an angle for propelling and mixing the grist as it passes through the said cylinder on its way to the mash-tun. This spindle is provided with driving pulleys. In mashing, the hot liquor, at a temperature of 160° F., is introduced into the sides of mashing machine in the form of a spray, at the same time the grist is allowed to fall from the grist case. The mash, as it is now called, is propelled, as before described, through the machine into the mash-tun.



The mash-tun itself is a circular vessel made of cast iron or copper, and provided on the outside with lagging and insulating material for the purpose of retaining the heat of the mash, while the top has a cover made with doors to lift up to give access to the tun (see Figs. 115, 116).

The interior of the tun is fitted usually with a machine known as a rake. This consists of a vertical shaft rising through the centre of tun, carried on a footstep bearing, and provided with driving gear.

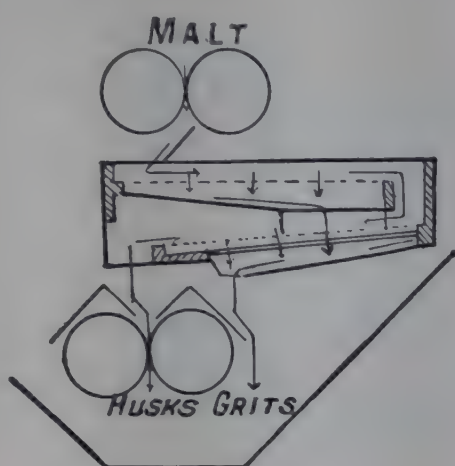


FIG. 112.—Diagram showing Method of Working in Seck Mill for usual Brewery purposes.

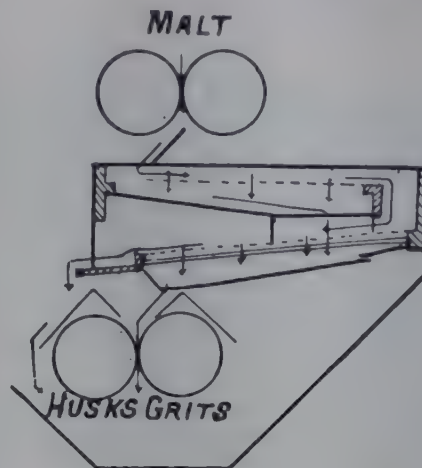


FIG. 113.—Diagram showing Slide in position for Regrinding Grits.

The end of the vertical shaft inside tun is connected by bevel gear wheels to a horizontal shaft which revolves on its axis, and at the same time travels round the interior of the tun. This shaft is fitted with a number of forks which are intended to stir up the mash and distribute it evenly over the interior of the tun. At about  $1\frac{1}{2}$  in. from the bottom of tun is fitted a slotted plate covering the whole surface area of the bottom, the slots being small enough to prevent any of the solid portion of the mash from going through, but large enough to allow the wort to percolate through, wort being the name given to the liquor at this stage.

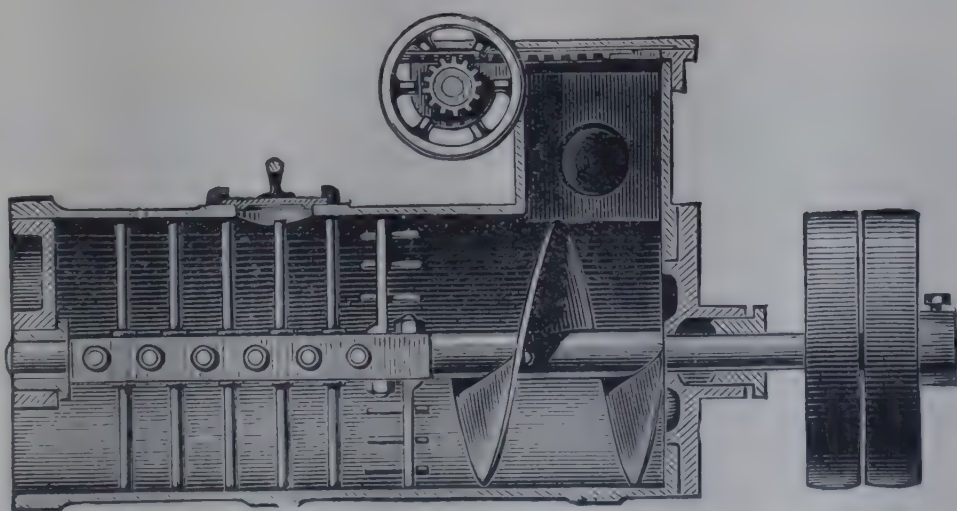


FIG. 114.—Llewellyns & James' Improved "Steel's" Mashing Machine. (Llewellyns & James, Bristol.)

In the early stage of mashing, **underletting** is sometimes resorted to, and this consists in introducing hot liquor into the bottom of the tun by means of pipes fixed at regular intervals in the actual bottom plates, and generally at some degrees higher temperature than is used for mashing. These pipes are also used for heating the tun before mashing. The mash is now allowed to stand for about two hours. The next process consists of washing out the wort from the mash (or "goods"). For this purpose an apparatus known as the **sparger**, which is fixed



inside the mash-tun at about the level of the top, is used, and consists of two perforated copper pipes, fitted to a revolving centre, and through which liquor is introduced. The perforations are at one side and bottom only of the pipe, the

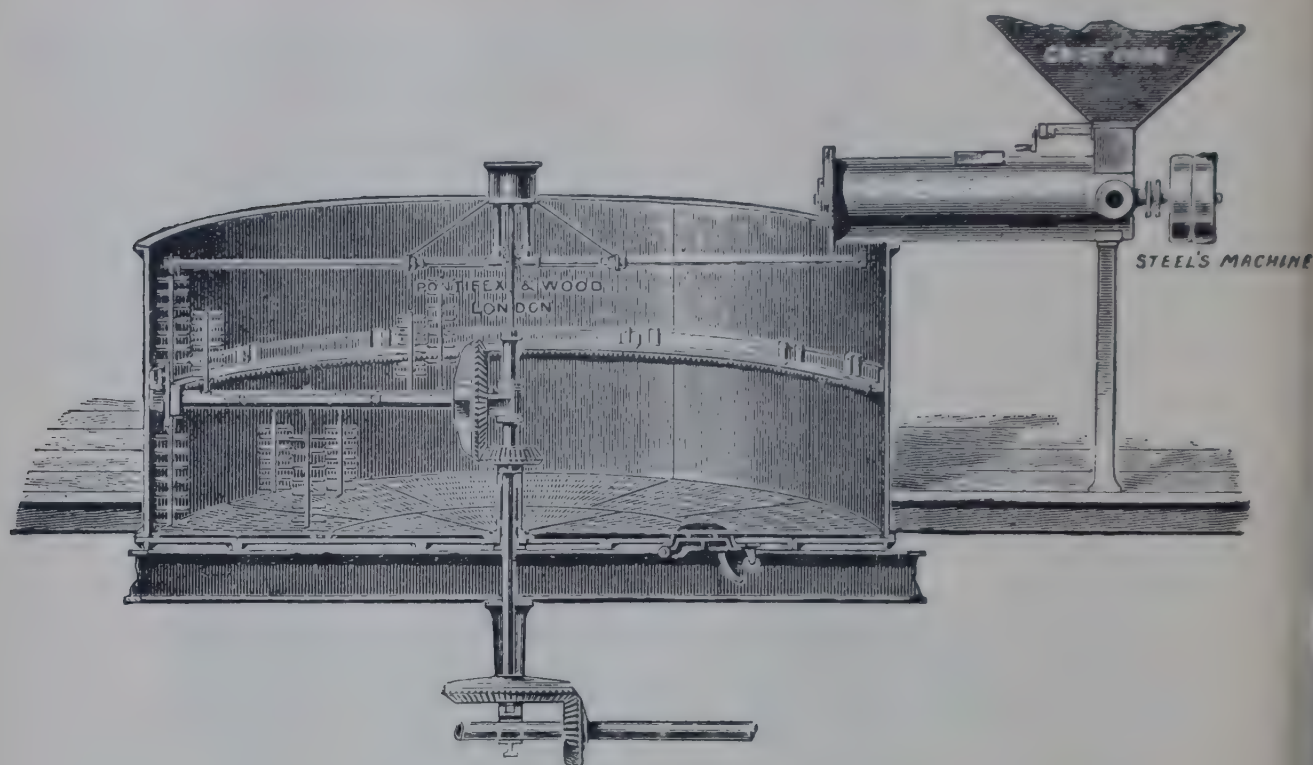


FIG. 115.—Cast-Iron Mash-Tun, showing Internal Rake Mashing Machine, Steel's Machine, Copper Sparger, Copper Slotted False Bottom, etc.  
(Haslam Foundry and Engineering Co., Derby.)

hot liquor flowing out acting as a driving power causing the pipes to revolve and distribute the hot liquor in a very fine spray over the goods. The sparging liquor has generally a temperature of  $170^{\circ}$ - $195^{\circ}$  F.

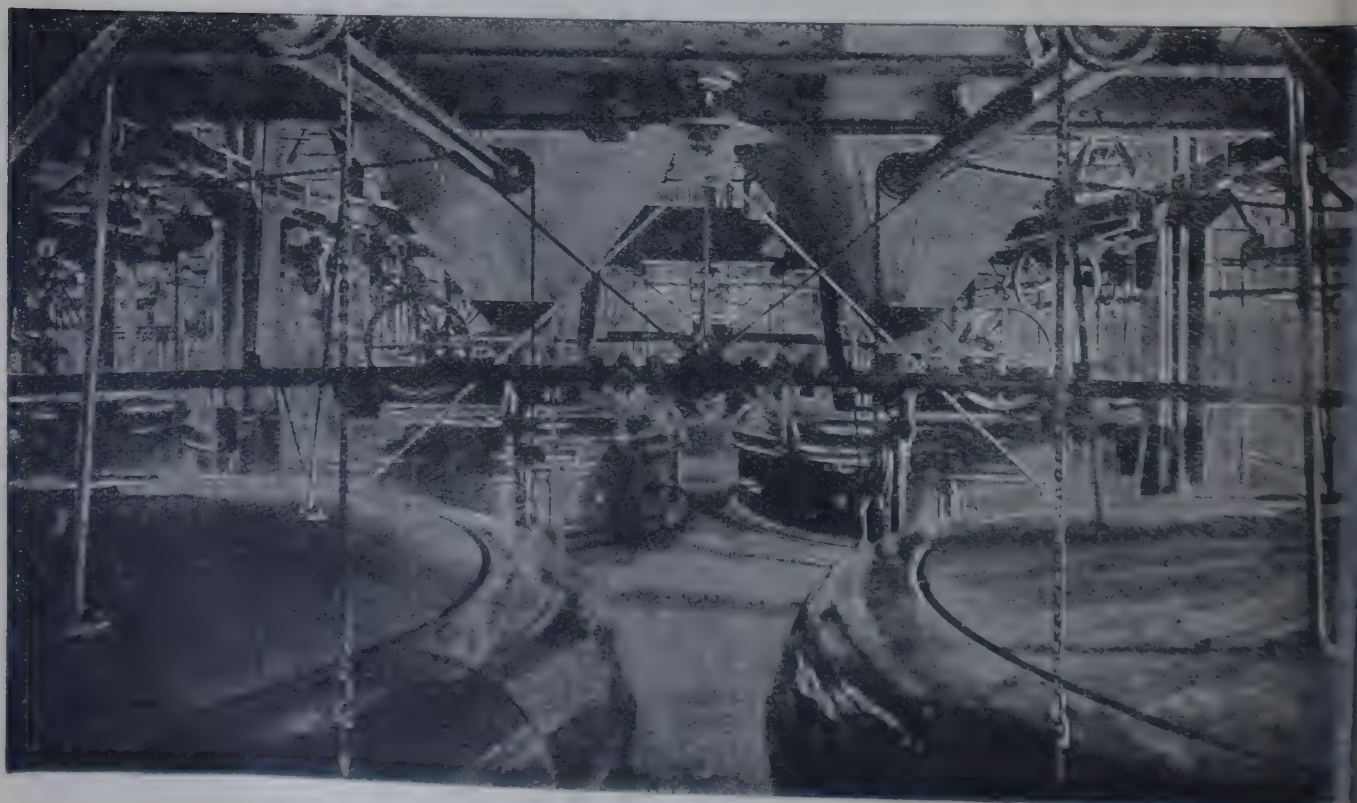


FIG. 116.—Mash-Tuns for Malt, at Guinness's Brewery, Dublin.



The wort is carried away by means of the pipes in the bottom of tun through a sampling pan, and by gravity direct to the underback and from thence to the copper. The **underback** is a vessel made either in cast iron or copper, and is provided as a source of supply to the copper, and as a means of safety, preventing the danger of burning the bottom of copper when finished wort is discharged. It is also used in some breweries for the purpose of continuing the action of the diastase after the wort leaves the mash-tun, and in this case is provided with either a steam coil or steam jacket for the purpose of maintaining the correct temperature.

In some breweries where raw grain is used, an apparatus called a "**Raw Grain Converter**" is often used (Fig. 117). It consists of a strong vessel heated internally by steam, as shown.

The malt and grits are mashed together in the apparatus, and when conversion is effected, let down into the ordinary mash-tun underneath, which simply acts as a filter; the wort is then pumped back into the converter and boiled, as in the ordinary copper, the hops being added in the usual way. The contents are again, after boiling, let down into the mash-tun, which in this instance acts as the hop back. The apparatus thus acts first as a raw grain converter, secondly as a mash-tun, thirdly as an ordinary boiling copper. No hop back is needed, as the mash-tun serves for this purpose.

The use of raw grain in the manufacture of malt liquor, provided it is wisely done, is stated to be decidedly advantageous to the quality of the beer produced, and is also very economical. With this apparatus as much as 50 per cent. of raw grain can be used, and it can also be used in lieu of the copper for boiling the wort.

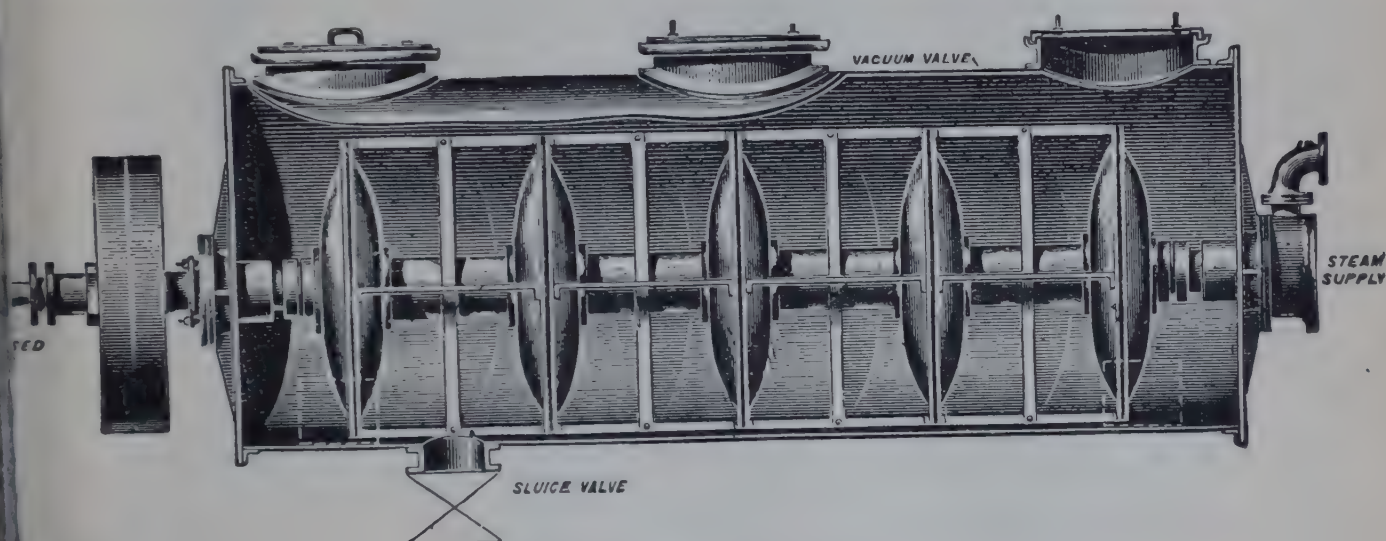


FIG. 117.—Raw Grain Converter.  
(Haslam Foundry and Engineering Co., Derby.)

**Boiling and Hopping the Wort.**—The **copper** is a vessel made in either cast iron or copper, principally the latter, and is heated either by a furnace underneath or by steam coils or steam jacket (Figs. 118, 119).

The wort having been run from the underback into the copper, is brought to the boil and the hops introduced at various intervals during the boiling period, the best hops being added last, so that the volatile hop oil is not all driven off. The amount of hops added to English ale and porters amounts to 10-15 lbs. per 1,000 gals., or, say, 10 lbs. hops for each quarter of malt. *German* brewers use far less than this, namely,  $1\frac{1}{2}$ -8 lbs. per 1,000 gals. The whole is allowed to boil generally for two hours and is then discharged into the hop back. This is a vessel large enough to contain the complete contents of the copper. It is made from cast iron or copper, and is fitted with a perforated false bottom fixed at  $1\frac{1}{2}$ -2 in. above the true bottom of the vessel. In this vessel the wort is allowed to stand for ten to fifteen minutes to allow the hops to settle on the false bottom, where they then form a filtering medium through which the wort runs off bright, the spent hops retaining most of the sedimentary matter.

**Cooling the Wort.**—The wort is now pumped for the first time by means of a three-throw pump up to the cooler, into which it is sprayed out through a perforated pipe or a spreader. This has for its object a partial aeration of the wort



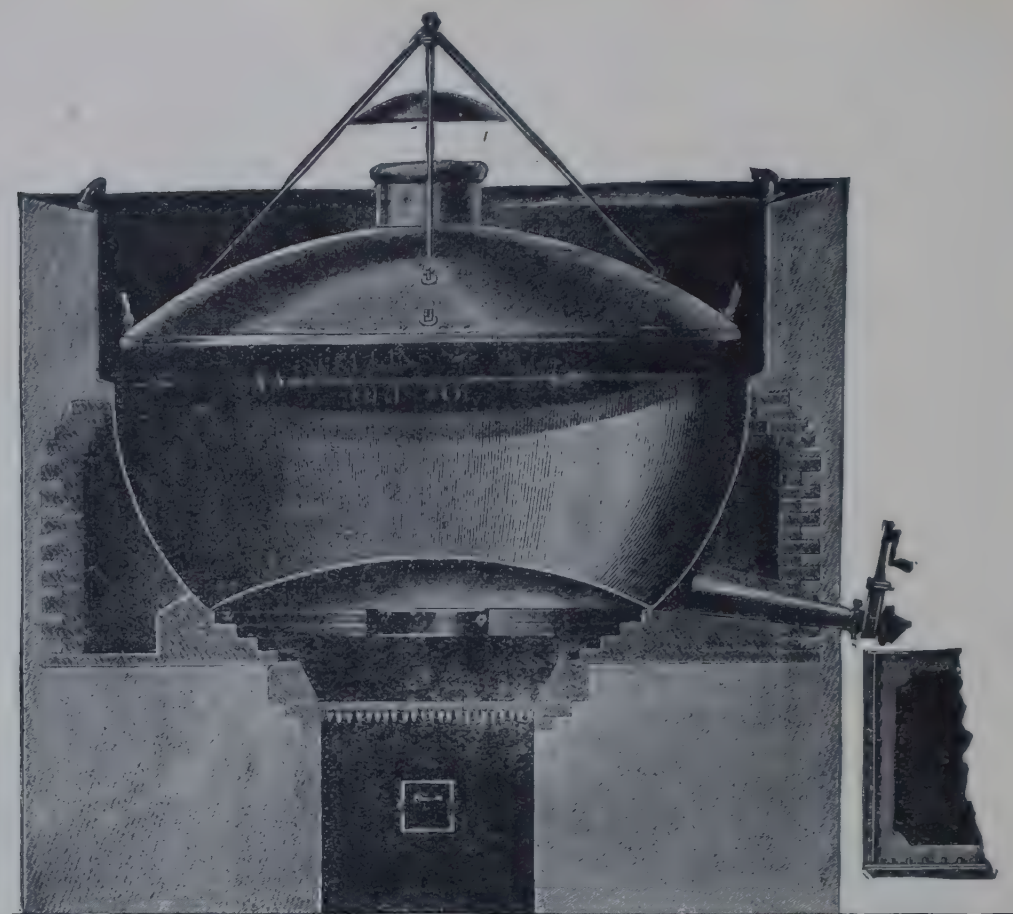


FIG. 118.—Open Fire Wort Copper. (Llewellyns & James, Bristol.)

before it settles into the cooler. The cooler is a vessel made of either cast iron, wood, or copper, and large enough to contain the whole of the contents discharged from the copper. The use of the cooler is partly to collect solid matter precipitated

by the aeration and drop in temperature, and to act as a source for regulating the supply of wort to the refrigerators or coolers situated immediately below. The refrigerator can be made either horizontal or vertical. The *vertical* type, as shown in Fig. 120, consists of a battery of copper tubes, one above the other, of such a shape to present a maximum of cooling surface to the falling wort. The inside of tubes receives a constant supply of cold liquor derived from the cold liquor tank, while the wort is distributed by means of a specially perforated pan at the top, which is regulated to allow a thin stream to trickle over the exterior of the tubes. By means of this arrangement it is possible to aerate and

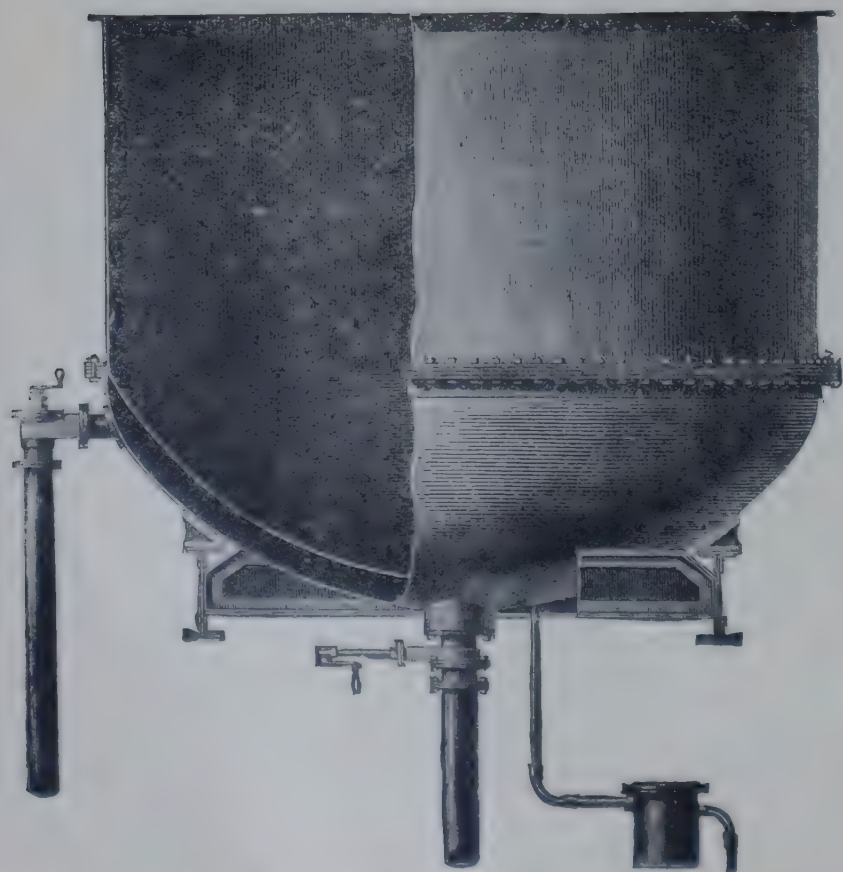


FIG. 119.—Steam Wort Copper.  
(Haslam Foundry and Engineering Co., Derby.)



cool the wort from the temperature in the cooler to the temperature at which it is desired to pitch or collect into the fermenting vessels. This is usually 56°-60° F.

**Composition and Analysis of the Wort.**—The strength of the wort is determined by taking its specific gravity at 17.5° C. This gives its concentration in sugar and the amount of malt extract.

Worts for light beers contain about 10 per cent. extract, heavier beers (*e.g.*, German *Bayerisch*) 12-14 per cent., while some English beers have worts containing 16-18 per cent. and more extract.

The duty on beer is levied at the rate (1910) of 7s. 9d. for each barrel (36 gals.) of wort at a sp. gr. of 1.055 (or, as in the trade, at a gravity of 1,055), an allowance of 6 per cent. being made for waste and loss during fermentation. The volume of the wort is measured by the excise officer in the fermenting vats or collectors before fermenting, the number of gallons of wort corresponding to each inch of depth of the vat being carefully gauged, and the number of gallons of wort actually contained in the vat is found by the dipping rod, a boxwood rule divided into inches.

If the wort has a greater gravity than 1,055 (*i.e.*, sp. gr. 1.055) it must be reduced to its equivalent in gallons at the standard gravity of 1,055. The calculation is made by multiplying the volume of brew in gallons by the excess of gravity over 1,000 (sp. gr. 1.000 = pure water) and dividing by 55. Thus suppose a brew of 4,000 gals. has a gravity of 1,060 (sp. gr. 1.060). Then  $4000 \times (1060 - 1000) = 240,000$ . This figure is divided by 55, the excess of standard gravity over 1,000. This gives  $\frac{240,000}{55} = 4327.2$ . That is, 4,000 gals. of wort of sp. gr. 1.060 are equivalent to 4327.2 gals. of wort

at the standard gravity of 1,055, and it is on this figure that the duty is levied, less 6 per cent. for waste deducted. A quarter of malt (336 lbs.) is supposed to yield four barrels of wort of sp. gr. 1.055.

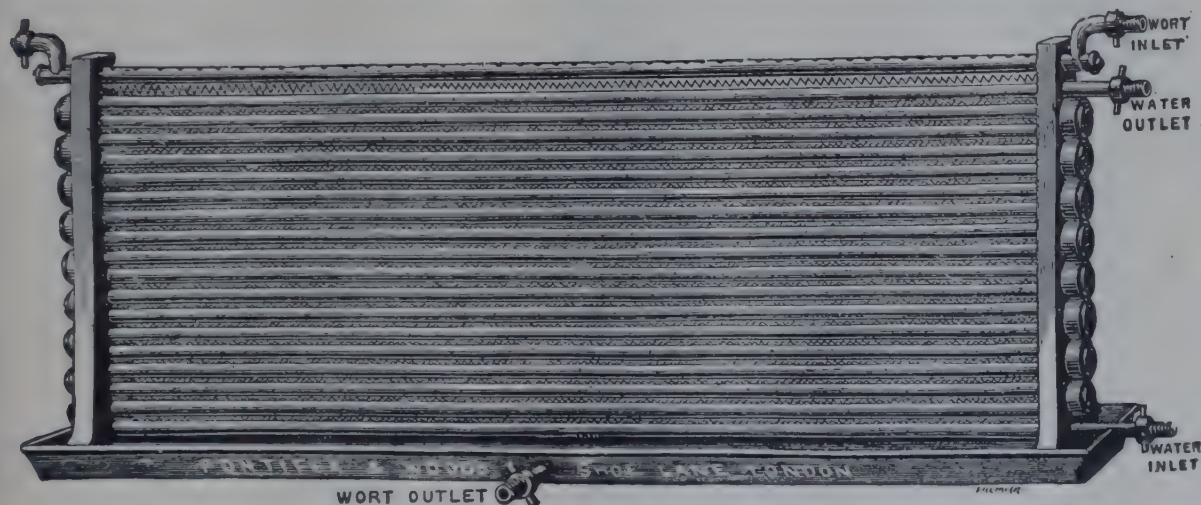


FIG. 120.—Refrigerator or Cooler.  
(Haslam Foundry and Engineering Co., Derby.)

The excise authorities reckon as equivalent to a quarter of barley (336 lbs.): 224 lbs. cane sugar; 256 lbs. glucose (invert sugar); 256 lbs. flaked maize or rice; 272 lbs. syrup No. 1, weighing 14 lbs. per gallon; 328 lbs. of syrup No. 2, weighing 13 lbs. 2 oz. per gallon.

The following is the composition of a typical wort:—

Specific gravity	-	-	-	-	1.056
Maltose	-	-	-	-	8.880
Non-maltose	-	-	-	-	4.82
Nitrogenous matter	-	-	-	-	0.830
Ash	-	-	-	-	0.234 with 0.085 P <sub>2</sub> O <sub>5</sub> .

Ratio of maltose : non-maltose = 1 : 0.54.

Everything that reduces Fehling's solution (alkaline copper sulphate solution) is counted as "maltose" on the basis of the reducing power of pure maltose. As a matter of fact, however, a considerable amount of the reduction arises from unfermentable dextrines, cane sugar, glucose, and pentoses, and no simpler method is known of differentiating between the individual effects contributed by the different sugars and the dextrines. The fermentability is best determined by actually fermenting the wort with yeast, and estimating the alcohol. Here, however, the difficulty is that different yeast races produce very different amounts of fermentation. The nitrogenous substances are principally peptones and amides, and are very important foods for the yeast. The ratio of maltose : non-maltose varies from 1 : 1 to 1 : 0.3.

**Fermenting the Wort.**—The cooled wort is now drawn from the pan in which the refrigerator stands into the top fermenting or collecting vessels. As soon



as the wort has started running into the collecting vessel, the yeast (which has first been thoroughly well roused and mixed in with some of the wort in a small separate vessel) is added. This is for the purpose of setting up the action of fermentation. When all the wort has been collected, it is allowed to stand until a yeasty head begins to form, the time required for this being in various cases from twenty-four to forty-eight hours. Immediately this head begins to form, the wort is run into the dropping fermenting vessel immediately below, leaving any extraneous matter in the top vessels, thus giving a cleaner wort for the final fermentation. For the purpose of removing the yeast thrown up by the fermentation an apparatus called a skimmer and parachute is provided. The skimmer is a wooden blade which passes over the top of the wort and just pushes the yeast

head into a parachute, which is a funnel-shaped vessel having a tube running through the bottom of the fermenting vessel into the yeast vessel below.

The fermenting vessels are also fitted with coils of pipe called attemperators through which cold and hot liquor may be run to raise or lower the temperature of the fermenting wort to the desired degree. This varies from  $56^{\circ}$ – $75^{\circ}$  according to the strength of the beer. The wort, which has now by the process of fermentation been converted into what we know as beer, is now ready for putting into casks. This part of the process is usually described as racking. For **Rate of Fermentation** see p. 240.

In England, where top fermentation is employed at a high temperature, the process usually lasts about eight days. In Germany, however, where "bottom fermentation" is almost exclusively employed, and the temperature is kept as low as  $5^{\circ}$ – $6^{\circ}$  C. ( $41^{\circ}$ – $43^{\circ}$  F.), the fermentation takes about twelve days.

The progress of the fermentation is followed day by day by the alteration in the specific gravity of the clear filtered wort, using the saccharometer for the purpose. On the Continent, **Balling's** saccharometer is employed, and it reads

directly the "apparent extract" as degrees "Balling," e.g., in the wort sample, p. 275, the "apparent extract" on the first day is 13.7, and on the twelfth only 6. The amount of "true extract" is also determined with the saccharometer, after removing the alcohol by boiling (the alcohol having a specific gravity less than 1), and making up the volume to its original amount with distilled water. In the wort sample on p. 275 it amounts to 7 on the twelfth day; and, consequently,  $13.7 - 7.0 = 6.7$  per cent. of extract has disappeared, having been converted into alcohol. Hence the "degree of fermentation" of the wort is:—

$$\frac{\text{loss of extract}}{\text{original extract}} \times 100 = \frac{6.7}{13.7} \times 100 = 49.0.$$

The storage period in cask varies to a large extent, some beers being sent out immediately after racking, and others being kept in cask for a long time, sometimes twelve or eighteen months or longer. Racking is mostly done in the cellars, which should be kept at an even temperature all the year round.

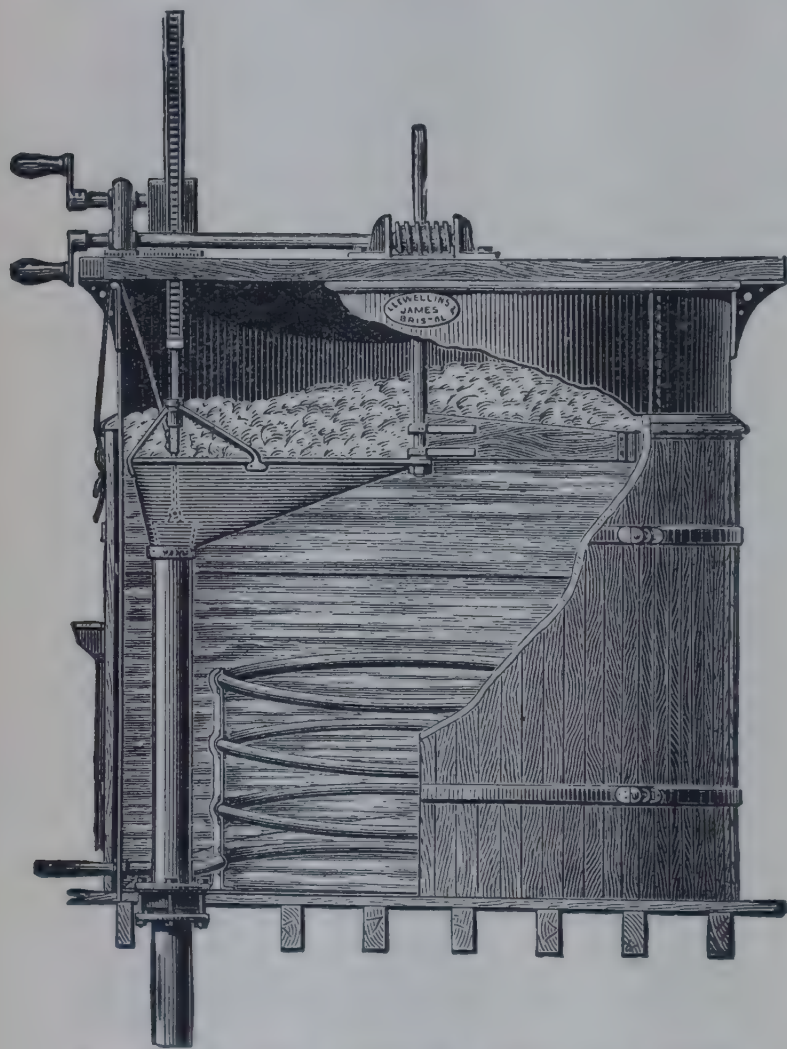


FIG. 121.—Copper Fermenting Round, with Jacketed Wood-Casing, Skimmer, and Parachute.  
(Llewellyn & James, Bristol.)



## ALTERATION IN A WORT DURING FERMENTATION

	Original Wort.	Eighth Day.	Twelfth Day.
Specific gravity - - - -	1.056	1.028	1.025
Per cent. Balling (apparent extract)	13.7	6.7	6.0
True extract - - - -	13.7	7.6	7.0
Alcohol - - - -	0	2.95	3.25
Maltose - - - -	8.88	3.34	2.19
Nitrogenous substances - - -	0.83	0.66	0.60
Ash - - - -	0.234	0.222	0.220
P <sub>2</sub> O <sub>5</sub> - - - -	0.084	0.079	0.078
Maltose : non-maltose - - -	1 : 0.54	1 : 1.27	1 : 2.10
Degree of fermentation - - -	...	44.5	49.0

The beer, or barm ale as it is called, is drained or pressed from the yeasts which have been skimmed off through the parachute into the yeast back, and is returned to the fermenting vessel, whilst the yeast, or such as is wanted, is carefully placed in a cool place for use in a future brew. The residues from the brewing operations are spent or exhausted grains, hops or yeast or, as it is commonly called, barm, and there are various markets open for these commodities.

In Germany a portion of the excess yeast is used for making yeast extracts (*Ovos, Siris*). More recently, prepared yeast has been placed on the market as human food, as a substitute for meat. For this purpose the yeast is freed from the bitter hop taste by treating with sodium carbonate solution. About 10,000 tons of yeast from German breweries can be utilised annually in this way.

**Bottled Beer** for export is usually pasteurised by heating on the water bath for a half to one hour at 50°-60° C. The use of antiseptics such as salicylic acid, boracic acid, saccharine, etc., for preserving beer is unnecessary, and, indeed, highly injurious.

A good percentage of alcohol, strong hopping, and perfect cleanliness in manufacture render the beer quite stable.

One great essential for successful brewing is cleanliness.

## FOREIGN SYSTEMS OF BREWING

### Manufacture of German Lager Beer

The general trend of brewing within recent times has been in favour of light, bright beers, containing less alcohol and hops than the older types of beer.

This trend has resulted in the almost universal production in Germany of beer, which is not only more palatable, but also less intoxicating and more easily digestible than most kinds of English beer.

German beer (termed "Lager" in English, but "Export Bier" in Germany, the term "Lager" being reserved in that country for a somewhat different sort of beer) is produced on entirely different principles from English beer. English beer is produced by a process of "Infusion," whereas German beer is the result of the "Decoction" system.

The process is as follows:—

**Mashing.**—The "grist," or ground malt, is mashed with cold water until thoroughly mixed, the temperature of the mash-tun being kept at 85°-100° F. by the addition of hot water.

One-third of the mash is then run into the mash copper (*Maisch Kessel*), and heated at 166° F. until the milky fluid becomes transparent, the starch being then rendered soluble by the diastase.

The **Dickmaische** (as the fluid is now called) is boiled for a quarter to three-quarters of an hour, then a portion run back into the mash-tun proper, so as to raise the temperature of the whole to 110°-125° F. After a few minutes another third is withdrawn and treated as before, forming the second **Dickmaische**. This is again returned to the mash-tun, and the whole thoroughly worked up, and allowed to stand, so that coagulated albuminoids, etc., may settle out. Then another third, which from its being a practically clear mash is called the **Lautermaische**, is withdrawn and thoroughly boiled to precipitate all albuminoids, and then again returned to the mash-tun, where the mashing is continued until the final temperature is just over 160° F. The hops are added, and the wort run off and cooled to a low temperature, and yeast added.

**Fermentation of the Wort.**—Here again the procedure differs entirely from the English practice. In the English *top-fermentation* system the wort is pitched and fermented at a relatively high temperature, viz., 55°-66° F. Moreover, pure yeast cultures cannot be used with success because the fermenting vessels are of great size, and present a large surface to the air for infection. Also the yeast comes to the top of the liquor and there develops (top-fermentation), forming the head. The primary fermentation is very vigorous and rapid, being complete in two to three days, while the secondary fermentation is (in the case of running ales at least) over in fourteen days. Consequently the high temperature and surface exposure of the yeast (which are essential features of the English system) cause infection by foreign yeasts, and a rapid deterioration of any pure yeast culture used results. Also it is generally believed that there is no single type of yeast which will produce characteristic English beer. The simultaneous action of several species of yeast are necessary. Hence in English breweries pure single yeast cultures have not been a success (although the use of *mixed* pure cultures has been more promising). Some breweries, however, have used them successfully. See "Brewery Infection and Pure Yeast," by R. L. Sian, *Journ. Inst. Brewing*, 1906, vol. xii., p. 118.

On the **Continental system**, however, all is quite otherwise. Here the yeast is a *bottom-fermentation* sort, and the pitching and fermentation takes place at very low temperatures in cellars cooled artificially to 37°-38° F., and the fermentation vats are small in area. The yeast formed in the fermenting wort (the temperature



of which is seldom above 50° F.) lies at the bottom of the fermenting tun (hence the name bottom-fermentation yeast).

All these conditions are eminently suitable for the employment of pure yeast cultures and the maintenance of it in an uncontaminated state. Hence the practice of brewing with pure yeast is universal in Denmark, Norway, Sweden, and is used in most of the breweries in Germany and Holland and in many cases in America.

After eleven to twelve days the primary fermentation of the yeast is complete, and the beer is stored in casks in an ice-cold cellar for one and a half to six months or more, according to the class of beer produced.

Nathan (German Patent, 135,539, November 1902) produces a good tasting beer in so short an interval as eight days by rendering the wort completely sterile in completely closed enamelled vessels, adding the yeast and blowing sterile air through the apparatus, whereby the yeast very rapidly develops. The process has excited much attention. For details see patent.

**Differences between English and Foreign Beers.**—It should be observed that the English beers, produced on the **infusion** system, contain more alcohol and are more stable than the German or **decoction** beers. The latter also contain more unfermented malt extract and so are more nutritive than English beers; they are also less heavily hopped and more heavily peptonised than English beers. Since they are produced at very low temperatures they hold in solution a larger amount of carbon dioxide than English beers.

English beers, however, are more stimulating and far more durable. For example "lager" beer cannot be kept on draught, and will not keep unless placed on ice. Consequently if a cask of **lager** beer is opened it must be rapidly consumed, for in a very few hours it becomes undrinkable, the gas rapidly escaping and the beer becoming flat and unpleasant. In Germany, therefore, every publican must have a supply of ice, which is frequently delivered by the brewery together with the beer.

Certain "alcohol-free" beers which are manufactured are either merely malt extract or very weakly fermented beers containing but very little alcohol.

**Composition of English and Foreign Beers.**—The following analyses will give a general idea of the different compositions of the various English and Continental beers:—

Beer.						Total Solids (Extract) per Cent.	Alcohol per Cent.
English Beers.	{	Pale ale	-	-	-	4.32	5.58
		Light bitter	-	-	-	3.96	3.34
		Stout	-	-	-	5.27	6.11
		Munich lager	-	-	-	6.95	3.40
German Beers.	{	" export	-	-	-	7.48	4.12
		Pilsener	-	-	-	5.10	3.49
		Berlin Königstadt (light)	-	-	-	4.19	5.28
		" (dark)	-	-	-	7.73	3.94
		Nürnberg (dark)	-	-	-	6.09	3.51
		Berlin weiss beer	-	-	-	4.21	2.82

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## V.—SPIRITS AND INDUSTRIAL ALCOHOL, INCLUDING DISTILLING PLANT

BY G. MARTIN, Ph.D., D.Sc., AND W. H. STEPHENS, A.R.C.S.

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(See also under *Distillation*, p. 295)

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**Uses of Alcohol.**—The greater part of the spirits now produced is consumed as a beverage in the form of brandy, rum, whisky, cognac, cherry brandy, etc. etc. Part, however, is used in making “liqueurs,” which are alcoholised wines.

Alcohol is also used on a very large scale technically for heating purposes (“methylated spirits”) in spirit lamps, for alcohol lamps, for motor engines, for the manufacture of ether, chloroform, chloral hydrate, glacial acetic acid, aniline colours, celluloid, xylonite, collodion, fulminating powder and explosives, transparent soap, synthetic camphor, artificial silk, synthetic aconite, belladonna, and other drugs, photographic emulsions, lanoline, vinegar, artificial lubricants, furniture polish, varnish, lacquers, enamels, quick-drying paints, dissolving resins for hat makers, goldbeaters’ skin, extracting vegetable alkaloids, etc. etc. It will be seen, therefore, that apart from its use as a beverage, alcohol is one of the most important chemicals, and its cheap production is absolutely essential for the development of many new industries. For such industrial purposes it is left tax free, but is made undrinkable by the addition of unpalatable substances (see *Denatured Alcohol*, p. 281). For such technical purposes Germany in 1904-05 used no less than 32,000,000 gals. of industrial alcohol, and the United Kingdom in 1908-09, 6,280,000 gals., while 440,000 gals. of alcohol (21,000 gals. being methyl alcohol) were used in a pure state in the manufactures, or for scientific purposes (hospitals, etc.).



The use of alcohol as a motor fuel, *i.e.*, as the explosive agent in an internal combustion motor, is a modern development of engineering practice. It is cleaner than petroleum, and far less dangerous to use than gasoline, but alcohol motors are difficult to start, and as a power producer it is slightly inferior to gasoline, and slightly dearer. Should, however, as seems probable, the price of gasoline rise, there is little doubt that alcohol motors will come widely into use, and great improvements in design are, no doubt, possible, since an explosive mixture of alcohol vapour and air can be used under far higher compression without auto-ignition than a similar mixture of gasoline and air. The heating value of alcohol lies between 13,310 and 10,080 B.T.U. per pound. The following table is instructive :—

MOTOR FUELS.

Fuel	Heating Value per Pound, B.T.U.	Cost per Gallon (1951).	Specific Gravity.	Cost of 10,000 B.T.U. approx.
Gasolene (Wholesale)	19,000	2s. 10d.	0.710	2½d.
Kerosene "	18,500	1s. 3d.	0.800	1d.
Alcohol (90 per cent.) -	10,080	2s. 1½d.	0.815	3¼d.

Alcohol lamps have a fairly extended use on the Continent, the colourless hot flame of the burning alcohol being used in the same way as our ordinary bunsen gas burners to heat an incandescent mantle. A very powerful light is thus obtained. Such lamps, however, have to be started by burning a little alcohol in a pan, thus heating the alcohol until part gasifies. They are not, therefore, so convenient as oil or gas lamps.

Undoubtedly the most extended use of industrial alcohol is for heating purposes, such as boiling water in small spirit lamps in the household.

The amount of alcohol (pure) consumed per head of the population of the chief countries of the world is shown by the following statistics :—

ALCOHOL CONSUMED PER HEAD OF POPULATION.

	In Brandy, Spirits, etc.	In Beer, etc.	In Wine.	Total.
	Litres.	Litres.	Litres	
England - - - - -	2.4	6.3	0.3	9.0
Germany - - - - -	4.0	4.8	0.6	9.4
France - - - - -	3.8	1.0	10.3	15.1
Austria-Hungary - - - - -	3.8	1.8	2.2	7.8
United States - - - - -	2.6	3.3	0.3	6.2
Denmark - - - - -	7.2	3.9	...	11.1
Sweden - - - - -	4.0	1.5	...	5.5
Russia - - - - -	2.4	0.2	...	2.6

The production of industrial alcohol, containing 80-97 per cent. of alcohol, first became a great industry when the stills were improved so that it became possible to obtain alcohol of this strength at a single operation directly from the alcohol-weak fermented mash. At the present time, especially on the Continent, the centre of gravity of the spirit industry lies in distilleries producing "silent spirit" of over 80-90 per cent. alcohol, and not in those directly producing whiskies brandies, etc., containing 20-60 per cent. of alcohol. The latter are now produced as a rule from "silent spirit" by suitable dilutions with water, etc.

The ordinary brandy, whisky, etc., contain from 20-60 per cent. of alcohol. In so concentrated a form the alcohol acts as a poison to the nervous system in a manner similar to opium or tobacco, producing at first a stimulating effect, which afterwards generates a craving for the drug, and causes the distressing effects of alcoholism which are matters of common knowledge.

Alcohol of more than 60 per cent. also produces poisoning by its dehydrating

effect. Small amounts of alcohol, such as exist in beer and wine, if taken in moderation, cannot be regarded as injurious to health.

The following statistics relating to alcohol are of interest as showing the progress of the industry in the chief civilised countries:—

**England** produced in 1906-07, 1,413,000 hl.,\* 100 per cent. alcohol (1 hl. = 220 gals.), principally grain alcohol.

The **United States** (1908-09), 2,647,000 hl., also principally from grain.

**Austria-Hungary** (1908-09), 2,647,000 hl. (from maize and sugar beet molasses).

**Russia** (1906), 4,182,000 hl. (half from potatoes, half from grain).

**France** (1908-09), 2,538,000 hl., principally from sugar beet, as shown in the following table:—

1,259,000 hl. (100 per cent.) from sugar beet.			
448,000	„	„	molasses.
363,000	„	„	potatoes and other starchy material.
212,000	„	„	wine.
256,000	„	„	apples, pears, wine lees, etc.

It will be seen that by far the greatest amount of spirits is in this case produced from the sugar beet, both from its sugar-rich juice and from molasses, the uncrystallisable residues of beet sugar factories. Potatoes play but little part in the industry. 3,000 industrial distilleries exist in France, and a very great number of small "farmer distilleries" (300,000).

**Germany** in 1908-09 produced 4,255,100 hl. (100 per cent.) of alcohol, as shown in following table:—

3,419,200 hl. from potatoes (from 6,400 "farmer" distilleries).	
408,900	„ grain (from 730 industrial distilleries and compressed yeast manufacturers).
291,700	„ grain in 6,600 "farmer" distilleries.
86,800	„ molasses (27 molasses distilleries).
48,500	„ fruit (apples, etc.), wine, yeast, etc., in 60,000 very small distilleries.

**Total** 4,255,100 in 74,000 distilleries.

As raw products, nearly 3,000,000 tons of potatoes, 293,000 tons of grain (rye, barley, maize), and 32,000 tons of molasses are used. Contrary to France, in Germany little spirit is produced from sugar beet or molasses. This was a consequence of the taxing of the mash capacity of the vats, which made the economic working of their mashes impossible. Since the vat tax (in 1909) has now been abolished, we see in Germany a great increase in the amount of alcohol produced from sugar beet and molasses.

Of the total amount of German alcohol produced, 2,651,000 hl. (4.2 l. per head) is consumed as a beverage, and 1,480,000 (2.3 l. per head) for industrial purposes. 175,600 hl. (100 per cent.) were consumed in the manufacture of vinegar, but the bulk of the industrial alcohol is used for burning purposes, spirit lamps, etc.

## Taxation of Alcohol

Distilled spirits when used as a beverage are subjected to very high taxation in all civilised countries, the taxation so greatly exceeding the cost of production that the whole industry is more or less completely dependent upon the particular excise laws of each country. In **England** (1950) a spirit duty of £10, 10s. 10d. per gallon of proof spirit is levied; the cost of production being only about 1s. 6d. per gallon. The revenue derived from this source in 1949 amounted to £46,721,370.

The number of distilleries at work throughout the United Kingdom in 1909 was 166 (England 8, Scotland 132, Ireland 26). The number of proof gallons retained for consumption in the United Kingdom was (1908-09) 32,000,000. In **Germany** the excise was until 1909 levied on the capacity of the fermenting vats, and consequently the German distillers work with as concentrated mashes as possible, up to 22°-25° Brix. In 1909 this mode of taxing the capacity of the vats ceased, and so the character of the German distilleries altered considerably after this relaxation. A duty of 105-125 m. per hectolitre was levied in 1910, the exact amount of duty varying with the *maximum* amount of alcohol given by each distiller every ten years—the larger the production the larger the tax. An additional tax of 4-14 m. protects the small "farmer distilleries" against the large industrial concerns—the larger the distillery the greater the tax. In 1910-11 in

\* 1 hectolitre = 100 litres = 22.01 gallons.



Germany the amount of spirits retained for consumption amounted to 1,780,000 hl. (2.7 l. per head). The duty levied on imported spirits is 275-300 m. per 1 dz.\* The total revenue raised in Germany by the spirit duty amounted in 1908-09 to 162,700,000 m. The cost of manufacture of 1 hl. of alcohol (100 per cent.) is 25-30 m. The selling price of the taxed fine alcohol is 150-175 m. per hectolitre. In the **United States** the number of distilleries operated is about 1,800. The capital invested in distilleries and the production of potable spirits amounted to \$50,101,000 in 1904, and to \$72,450,000 in 1909 (increase, 45 per cent.). The value of the products increased from \$131,270,000 (1904) to \$204,699,000 (1909). The import of distilled spirits amounted in 1910 to \$7,228,000, on which a duty of \$9,116,000 was raised (126.12 per cent.).

## Denatured Alcohol

Alcohol for industrial purposes† is now duty free in most countries including England. The tax on such alcohol for many years most injuriously affected the industry in fine chemicals in England. To such alcohol, however, substances must be added so as to make it undrinkable. The substances added must be of such a nature as to render their removal very difficult by simple operations. In England **completely denatured alcohol** (mineralised methylated spirit) is made by adding 1 part of wood naphtha to 9 parts of grain alcohol (50 per cent. *above* proof), and to the mixture 0.385 per cent. of mineral naphtha (petroleum of sp. gr. not less than 0.800). In the U.S. the denaturing mixture is  $\frac{1}{2}$  vol. benzine + 10 vols. methyl alcohol to 100 vols. ethyl alcohol. Completely denatured alcohol is allowed to be sold only by licensed retailers for general use (but not for making beverages or medicines).

**Incompletely denatured alcohol** (industrial methylated spirits) consists of not less than 5 per cent. of approved wood naphtha or other substance or combination of substances approved of by the Commissioners of Customs and Excise.

The wood naphtha used must be so impure as to render undrinkable alcohol to which it has been added. It must contain *not less* than 72 per cent. by vol. of methyl alcohol, and *not more* than 12 g. per 100 c.c. of aldehyde, acetone and ketones (estimated by Messinger's iodoform process as acetone) nor *more than* 3 g. of esters (estimated as methyl acetate by hydrolysis). At least 5 c.c. of N/10 acid must be necessary to neutralise 25 c.c. of the naphtha; not more than 30 c.c. of the naphtha should decolorise 0.5 g. of bromine in aqueous solution.

Industrial methylated spirits can only be purchased for manufacturing operations from a methylator. Specially denatured alcohol, suitable for particular industries, is allowed in cases where the presence of the above-mentioned denaturants would be injurious. The United Kingdom produced in 1908-09 of industrial methylated spirit, 3,884,740 proof gals. and 2,395,306 gals. of mineralised methylated spirit.

In **Germany** the usual denaturing agents for ordinary alcohol used for burning purposes is 2 per cent. by volume of wood spirit +  $\frac{1}{2}$  per cent. by volume of pyridine bases; or a mixture of benzol and light petroleum. In alcohol used for the manufacture of acetic acid the addition of acetic acid is allowed as a denaturant. Alcohol used for the manufacture of **ether** and **collodium** is denatured with 10 per cent. ether or camphor. To alcohol for varnishes  $\frac{1}{2}$  per cent. turpentine is added.

## Benefits of Industrial Alcohol to Agriculture

Alcohol can be produced in practically unlimited quantities from a great variety of farm produce, so that every kind of soil and climate can be utilised. It can even be made from spoiled crops, corn stalks, refuse, etc. The alcohol so produced furnishes a cheap and excellent motive power of engines, and no doubt, after the exhaustion of the coal and oil supplies of the world, will be the ultimate fuel of mankind. For sunshine only is required for the production of the starchy materials from which alcohol is produced, and there is no exhaustion of the soil in the process. Only carbon, hydrogen, and oxygen are withdrawn from the air under the influence of sunlight, and, after the combustion of alcohol, they come back again as carbon dioxide and water. The nitrates, phosphates, lime, etc., absorbed from the soil by the growing vegetation, all remain in the immediate neighbourhood in the liquid wash from which the alcohol has been distilled off, and being used as fodder, are returned to the ground as manure.

In England and U.S.A. the bulk of the spirits produced is manufactured from grain. This was also the case in Germany one hundred years ago, but now, in that country, the bulk of the spirits is produced

\* 1 dz. = 100 kilograms =  $\frac{1}{16}$  ton.

† See *Journ. Soc. Chem. Ind.*, 1915, 34, 53.

from potatoes, which give a heavier and cheaper yield of starch per acre than any other vegetable and enable a very pure spirit to be easily obtained. In Germany, too, the manufacture of spirits is of very great benefit to agriculture, for it is carried on by the mutual co-operation of farmers, who sow their own potatoes and then cart them to a joint-owned distillery, where they are converted into alcohol in the winter months (up to May), while the spent wash and residues, rich in nitrogenous matters, is utilised as a cattle-food on the farms.

Consequently hand in hand with the production of alcohol there goes on an extensive breeding of cattle, which again produce the manure necessary for the continuous cultivation of crops. In 1906 no less than 71,000 of these so-called "farmer distilleries" were in operation. Besides these, however, were about 1,000 industrial distilleries, usually situated in or near a town, many of such distilleries specialising in the manufacture of yeast as described under that heading.

Four kinds of distilleries may be recognised:—

1. Those producing alcoholic beverages containing 25-60 per cent. of alcohol. In this class come the whisky and brandy manufacturers.

2. Those producing absolute alcohol up to 80-95 per cent., such alcohol being in too concentrated a form for drinking purposes. Under this heading may be classed the German potato distilleries, the great maize and molasses distilleries, and generally, manufacturers of industrial alcohol.

3. Alcohol rectifiers, where the crude 80-95 per cent. alcohol is redistilled and purified.

4. Compressed yeast manufacturers. In these distilleries the main object aimed at is the production of yeast, the spirits being produced as a by-product.

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## RAW MATERIALS USED IN THE PRODUCTION OF SPIRITS

Although alcohol can be obtained from the ethylene,  $C_2H_4$ , contained in coal gas, or directly from acetylene,  $C_2H_2$ , from calcium carbide, by means of concentrated sulphuric acid, yet in practice it is almost invariably obtained from sugar or starch, although attempts, attended with a certain amount of success, have been made to produce alcohol from wood cellulose. (See **Alcohol from Wood**, p. 294.)

The raw materials for the production of spirits may be divided into three great classes, as follows:—

**1. Alcohol-containing Materials.**—In France, Spain, Italy, and in fact all lands where wine is produced on a considerable scale, spirits are produced by distilling wines or wine lees. Such spirits are known as brandies, and are much valued on account of their pleasant aroma, due to wine fusel oils. Genuine **brandy** is obtained by distilling wine in small pot stills. The best brandies, called Cognacs (Charente and Charente Inférieure) from the districts in which they are made, are of a peculiarly fine and delicate character, and fetch 1,000 francs per hectolitre. They are made from light white wines possessing no marked bouquet. They are used for adding to champagne. The fuller and more aromatic wines of Burgundy and the Gironde do not yield such good brandies. A large amount of brandy is also made by adding water to wine lees (*i.e.*, the pulp of skins, pips, wine yeast, etc., remaining in the wine-press) and distilling. Artificial cognac oils (see p. 251) are largely manufactured for adding to cognacs. Brandies improve with age.

**2. Sugar-containing Materials.**—It is also possible to produce alcohol from sacchariferous substances, such as sugar beets, figs, amber cane, and especially the residual molasses from sugar manufacture. As these substances already contain sugar they do not need the mashing process necessary with starchy raw materials, and may therefore be ground up and directly fermented with yeast. France produces more than one-third of her spirits from the fermented juice of the sugar beet. In Portugal the carob bean (St John's Bread) is fermented and distilled, and in Brazil strawberries. In Jamaica and Cuba molasses and sugar-rich residues, such as cane-megasse, from the manufacture of cane sugar are allowed to spontaneously ferment, and then are distilled for **Rum**. Fictitious **rums**, however, are now made from alcohol flavoured with essential oils ("rum essence"). Rums contain 50-60 per cent. of alcohol, and sugar is often added. **Arrak** is produced in Java in a similar manner from the cane sugar and the sugar-rich juice of the sugar palm, which is allowed to ferment, either spontaneously or with the addition of certain rice yeasts.

**Cherry brandy** and **plum spirits** are produced by distilling fermented cherries or plums and contain oil of bitter almonds and a trace of hydrocyanic acid.

**Gin** is obtained by distilling plain spirit in the presence of flavouring agents, such as juniper, angelica, cinnamon, sweet fennel, coriander, etc. Flavouring agents are often added after distillation. Sweetened gin contains 3-6 per cent. of sugar.

In short, all sweet fruit juices of kernel and other fruits (apples, pears, melons, figs, raspberries, strawberries, rowan berries, etc.), when mixed with sugar, and fermented and distilled, yield brandies of various aromas.

**3. Starch-containing Materials.**—Corn and potatoes form by far the most important alcohol-producing materials. In *England* most of the spirits are made from wheat, barley, and rice. Scotch whisky is made from malted barley. In

*Germany* nearly 80 per cent. of the total amount of spirits manufactured is made from **potatoes**, the remainder being made from wheat, rye, and maize, with the simultaneous production of compressed yeast. In *France* beet molasses and wine form the principal source of spirits, potatoes and corn contributing little to the total amount manufactured. *Hungary* and the *United States* make a large amount of spirits from **maize**, and *Russia* from rye. The use of potatoes, however, is extending in these lands, especially in Hungary and Russia—nearly half the spirits produced by the latter country now being manufactured from potatoes.

In hot countries a potato (sweet potato, Carolina potato), which also contains, besides starch, a considerable amount of sugar, is an important raw material for the manufacture of spirits. It is cultivated in Brazil, the West Indies, the Azores, Algiers, etc. etc.

**Potatoes** contain 16-24 per cent. starch, 1.95 per cent. nitrogenous substance, and 75 per cent. water. Recently potatoes have been put on the market in a dried powdered form. 100 parts of dry potatoes contain: Starchy matter, 70-78 per cent.; protein, 6 per cent.; water, 9-18 per cent. **Maize** contains on the average: Starch, 68 per cent.; moisture, 13 per cent.; protein, 10 per cent. **Wheat** contains 50-70 per cent. starch, and 7-21 per cent. protein. **Oats** contain 58 per cent. starch, 10 per cent. protein. **Rye** contains 68 per cent. starch, 11 per cent. protein.

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## THE MANUFACTURE OF SPIRITS

In a grain or potato distillery three and sometimes four main operations take place, namely:—

1. **Mashing**, *i.e.*, the conversion of starch into sugar by means of specially prepared malt.

2. **Fermenting and yeast production.**

3. **Distillation of the alcohol**; and, sometimes,

4. **Refining the alcohol by redistillation.**

In brandy and molasses distilleries the mashing process and malt preparation is unnecessary. Only the fermenting (2) and distillation (3) takes place.

The main operations of the brewer and distiller are identical in that both convert starch into sugar by means of diastase, and sugar into alcohol by means of yeast. But otherwise the method of operation in the two cases differs considerably. Thus the brewer seeks to produce **beer** which contains only a small amount of alcohol and has other constituents, such as the dextrines, flavouring principles, etc., of equal importance. He does not, therefore, completely convert his starch into maltose, otherwise a very thin beer, lacking body and palate, would result. But the distiller's object is to produce **alcohol** as such, and with this aim in view he carries his fermentation as far as possible, converting as much as possible of his starch into sugars, avoiding the formation of dextrines and fermenting these into alcohol.

The colour of the grain and the nature of the husk—which are of vital importance for the production of a palatable beer—matter little to the distiller, provided only that the grain is sound, contains a high percentage of starch and nitrogenous matter—the latter being necessary because much nitrogen-rich diastase must be produced.

Barley intended for distillers' malt is cleaned, graded, and steeped for a period ranging from two to four days, a somewhat longer period than is usual for brewing barley. The steeping water is usually liberally treated with antiseptics (bisulphite, lime, etc.) to prevent the development of bacteria which may subsequently injure the fermentation. The brewer has no necessity to use antiseptics at this stage, as any such bacteria, if developed, are later destroyed when the wort is boiled and hopped. The distiller, however, cannot boil or hop his wort and so must take every precaution at these early stages to avoid bacterial infection. The danger is especially great when maize is used for malting.

**Malting Operations.**—In Scots pot-still whisky distilleries, where nothing is used except barley malt, the process of malting is carried out as in brewing (which see), the flooring period, however, being slightly longer. In grain and potato distilleries, however, barley malt is used *not so much* as a source of alcohol as a source of the **diastase** to convert the starch of the grain or potatoes used in bulk for starch. Consequently in such distilleries the malt is grown in such a way as to contain a *maximum* of diastase. This, as the researches of Hayduck have shown, is attained by allowing the malt to germinate on the floor for a twenty-day period (in contradistinction to the brewing period of seven to ten days—"short malt"), since the mass of the diastase increases greatly with the progress of the growth of the malt. Such malt is known as "Long Malt," the seven to ten day malt used in brewing being known as "Short Malt." It is obvious that the longer the malt grows the greater will be the loss of starch (which is converted into CO<sub>2</sub> and sugars by the growing plant). In "Short Malt" the loss of starch amounts to about 6½ per cent. of the starch originally present, but in "Long Malt" the loss rises to 17 per cent. In other words, we obtain 100 parts of **short malt** for every 90 parts of **long malt**. Nevertheless, the 90 parts of the long malt contain as much **diastase** as 117-144 parts of short malt, so that in spite of the greater starch loss,



the preparation of long malt is of great advantage, enabling the distillers to effect a great saving in malt, sometimes as high as 50 per cent. Hayduck has shown that the relative diastatic strengths of **short** (seven to ten days) and **long** (twenty days) malt are:—

For heavy barleys 1 : 1.285.

For light barleys 1 : 1.605. (Hence the advantage of using small grain for distillers.)

Consequently the **long malt** process is employed in all modern distilleries. To produce it the grain is subjected to a lengthy steep until it absorbs 40-45 per cent. of water. It is then subjected to a very prolonged flooring of about twenty days at a moderate temperature (which should never exceed 63.5° F.). The development of mould fungi and bacteria is prevented by soaking the malt grain in dilute milk of lime (1 part of lime : 100 parts barley).

In contradistinction to the brewer, the distiller prefers **green** malt rather than **kilned** malt, because green malt possesses about twice the diastatic strength of kilned malt; the distiller regards his malt merely as an agent for saccharifying his starch and consequently will use as little kilned malt as possible. To the brewer, however, too much diastase is a positive disadvantage, as he does not want to completely convert all his starch to sugar, and the process of kilning is necessary to restrict the diastatic power of the malt and impart flavour to the beer. It should be noted, however, that the malt whisky distiller relies to a great extent on the kilning process for the development of the peculiar flavour of Scotch or Irish whisky, and consequently can only make a limited use of green malt. Also compressed yeast distilleries find that a certain proportion of kilned malt is necessary. Indeed, in hot weather it is often difficult to obtain a good supply of green malt as it will not bear carriage for any distance. Hence when the distiller finds himself unable to use green malt, he resorts to a malt which has been kilned at the lowest possible temperature.

### Other Kinds of Malt

The diastatic power of malt made from various kinds of corn is given in the following table:—

Barley malt	-	-	-	-	-	-	-	1.00
Oat malt	-	-	-	-	-	-	-	0.30
Maize malt	-	-	-	-	-	-	-	0.28
Rye malt	-	-	-	-	-	-	-	0.93
Wheat malt	-	-	-	-	-	-	-	1.08

Wheat malt is too costly for general use.

In spite of the low starch-transforming power of oat malt, it is used on a considerable scale, usually mixed with barley malt, because the zymase content of the yeast is considerably increased by the addition of the oat malt, and it acts very rapidly in the mash-tun. Maize malt is used for spirit manufacture in countries where barley is expensive. Rye is malted with barley or oats.

**Diastase from Fungi—The Amylo Process.**—In large corn distilleries in France, Belgium, and Hungary utilisation is made on a large scale of the diastase-secreting fungus, *Amylomyces Rouxii*, instead of malt. A sterilised corn (usually maize) mash contained in a closed vessel is inoculated with a very small quantity—one-tenth of a gram is sufficient—and filtered air is blown through the fluid for twenty hours. The mould develops very rapidly and converts the starch. Then pure yeast culture is added, and fermentation proceeds on ordinary lines. Although the mould is itself capable of fermenting the sugar itself, the yeast acts more rapidly and gives a greater percentage of alcohol. Hence both act together, the mould transforming the starch into sugar and the yeast and sugar into alcohol. One gram of culture transforms 25 tons of corn, and saves 3 tons of malt and 1 ton of starch used in the malting. Moreover, the mash is sterilised and worked in closed vessels, so that undesirable bacteria, etc., cannot develop—which is a great advantage. Technical difficulties have prevented the application of the mould to working potato starch. Another mould fungus, *Eurotium oryzae*, from Japan, saccharises starch exactly like malt. It contains diastase, which can be extracted with water and added to the mash to be converted (see pp. 226, 249).

### Theory of Mashing for Spirits

The brewer does not seek to completely transform all his starch into sugar. He must have in his wort a certain proportion of dextrine and similar non-ferment-



able carbohydrates, otherwise his beer will be thin and poor. Moreover his wort, before fermenting with yeast, is hopped and then sterilised by boiling. Quite otherwise is it with the distiller. He desires to convert his starch *entirely* into fermentable sugars (to obtain a maximum yield of alcohol), and he cannot sterilise the wort so obtained by boiling before adding the yeast for the following reasons. In the first place mashing should be carried out at low temperatures in order to allow the diastase to act more powerfully than in the case of brewers' wash, and in the second place the diastase is allowed to act during the period of alcoholic fermentation. If the wort were boiled before adding the yeast the diastase would be destroyed (as it is in brewing), and so the diastase could not act during the period of alcoholic fermentation, and a large proportion (as in brewing) of the starchy carbohydrates would remain in an unfermentable condition. It must be understood that low-temperature mashing will not alone completely transform starch into fermentable sugars, being converted into dextrines which are not further converted by diastase alone, but require the combined action of **yeast** and **diastase** to break them down completely into fermentable sugars. Hence it is that the distiller cannot boil his wort, and so sterilise it (as in brewing), because he would completely destroy his diastase. This puts the distiller in a very disadvantageous position as compared to the brewer, as unsterilised wort forms an excellent medium for the growth of undesirable bacteria. He must therefore forego the full advantage of low-temperature mashing and heat the mash to a temperature which is unfavourable to the development of bacteria. He first heats the mash very rapidly to 130° F., when maximum saccharifying action takes place, and keeps it at this temperature for a little time. Then he heats rapidly to 144° F., when the maximum liquefaction of the starch takes place, and finally he heats to 150°-154° F., when most of the undesirable bacteria, etc., are destroyed, while the diastase is not seriously injured in the presence of the large amount of sugar which has been formed, since Delbrück and Pätzold have shown that diastase in solutions rich in sugar can withstand a temperature as high as 154° F. without being very much weakened, while in a very weak sugar solution it is seriously injured at 146°.

**Preparation of the Mash.**—In the manufacture of whisky and other grain spirits, as carried on in the United Kingdom, the mashing apparatus is very similar to that used for brewing. The starchy matter, however, is more thoroughly extracted than is desirable in brewing by making several (Scotland, three; Ireland, two) successive mashings with the ground malt, the liquor from the last mash being used for mashing the next lot of malt.

In potato and maize distilleries, however, the mashies are made on a different principle; their starch must be gelatinised by steaming, and malt is only used as a source of diastase for converting the starch into sugar, and not as a source of starch. 100 parts of potatoes require 4-5 parts of green malt, while 100 parts of maize require 9-10 parts of green malt. Usually a small malting is run in connection with the distillery in order to produce the green malt fresh as required, since it will not keep.

The potatoes are washed and placed in a conical shaped boiler, known as a Henze steamer or "High Pressure Converter." This contains at its upper end a manhole for charging with potatoes, and steam pipes, carrying high-pressure steam, are supplied at the top, sides, and bottom. The apparatus is also supplied with an air-cock at the top, water-cock at the bottom, and a blow-out valve at the bottom, whereby the potato wash is blown into the fermentation vats. The apparatus is charged with potatoes and nearly filled with water. Steam is then allowed to enter through the upper inlet pipe, the air-cock and lower water-cock being left open until all the air is displaced and much of the condensed water has run off. The air-cocks and water-cocks are now closed and steaming continued until the internal pressure has risen to 2 atmospheres, the water-cock being opened from time to time to allow the condensed and amniotic water to run off—the last drawn amniotic water contains starch and is run into a preparatory wash vat. The upper steam



valve is now closed and steam driven in through the lower inlet pipe until the pressure reaches 3-4 atmospheres; the apparatus is kept at this pressure for ten to fifteen minutes, then the lower steam inlet pipe is closed, while the upper inlet and blow-out valves are opened and the apparatus blown out. The sudden release of the pressure causes the superheated water and steam in the potatoes to explosively expand, and reduces them to a mash in which the starch is (all but 2 per cent.) completely gelatinised and dissolved. The blowing out lasts forty-five

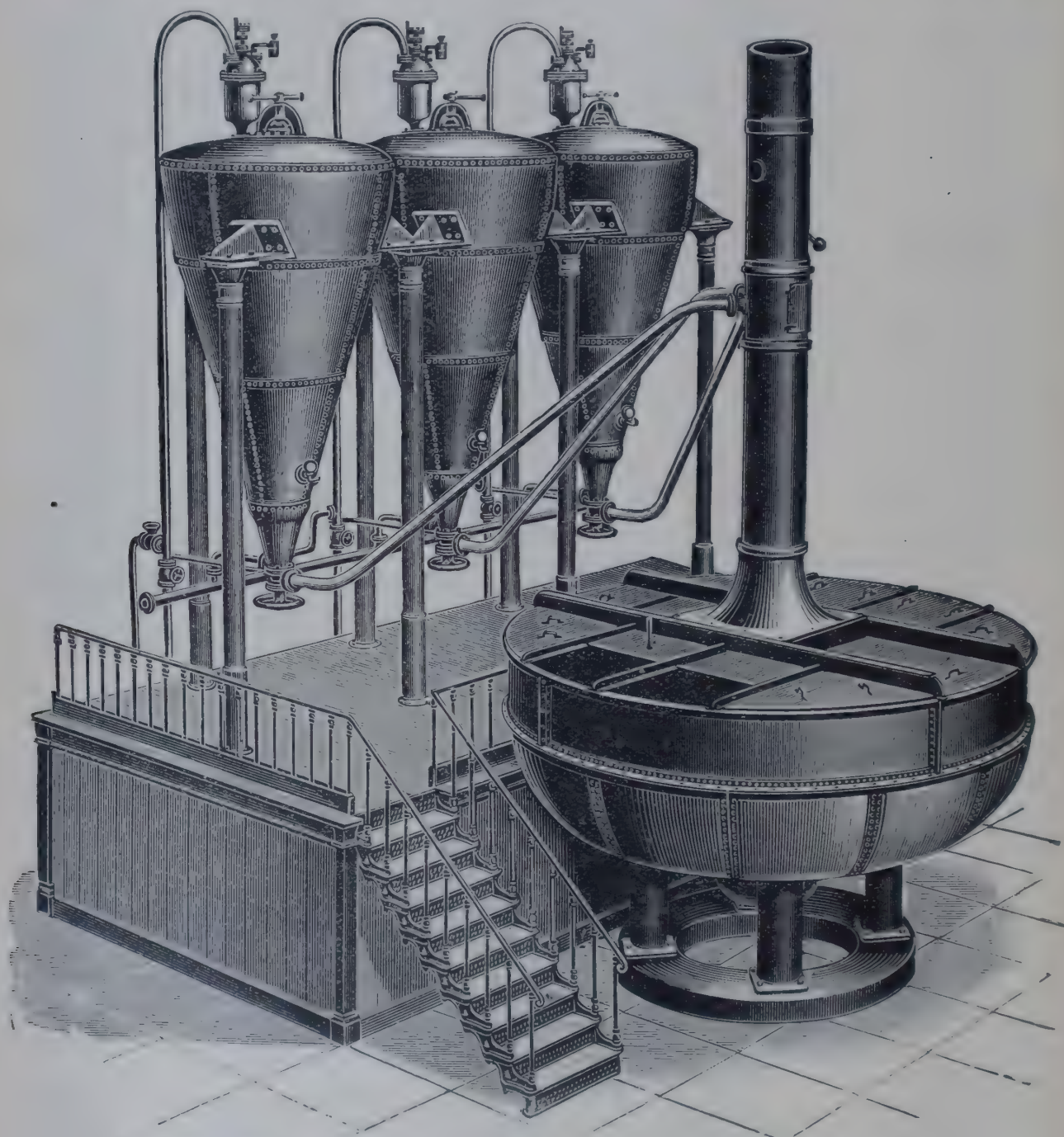


FIG. 122.—High-Pressure Converter or Steam Cookers (Henze Steamer) with Mashing Vats for Potatoes, etc. Llewellyns & James, Bristol.)

to fifty minutes, the potato mash being forcibly driven through the conical end of the boiler into the mashing vat.

When the maize is to be treated, the whole corns are fed into the converter or Henze boiler with the addition of some water and steamed three hours at  $3\text{--}3\frac{1}{2}$  atmospheres. The mass must be continually stirred, and this is achieved either by a stirring apparatus or by blowing in steam tangentially through a number of holes in the body of the apparatus. Just before blowing out the pressure is increased to 4 atmospheres and the contents blown forcibly out at the bottom of



the boiler through the blow-out pipe, which is provided with a grating and a comminuting valve consisting of a cone-shaped tube with sharp screw edges and corners. The mass is blown forcibly against the sharp corners and the corns are smashed up, while the superheated steam and water in the corn grains, suddenly expanding under the reduced pressure, blow the grains into a pulp and gelatinise their contained starch. This treatment completely disintegrates maize. Since at these high temperatures and pressures carbohydrates begin to decompose and turn brown, *Mandl* steams **ground** maize in an open Henze steamer, and then blows out with compressed air at 4-5 atmospheres. The mash is quite white.

The mashing and cooling vat (Fig. 124) consists of a stout iron vessel provided with a powerful screw at the bottom and a cooling system of copper pipes, through which cold water is driven. The hot mash pouring into the vessel is hurled by the screw against the sides and cooling pipes and is rapidly cooled to the proper temperature. The apparatus is furnished with a funnel provided with an exhaustor in the form of a steam jet situated in the funnel. This causes a rapid evaporation and consequent cooling of the hot mash, and also accelerates the rate at which the hot mass pours out of the steamer into the vat. The condensed water from the jet runs off through a pipe.

The method of mashing is as follows:—

The calculated amount of finely ground malt for the saccharisation of the mash is placed in the mash vat with a little water, and while the mass is thoroughly agitated the hot mash from the Henze steamer is slowly blown into the vat. The blowing out is regulated by the exhaustor and the amount of cooling water, so that the temperature of the mash in this operation is maintained at 130° F.

About five-sixths of the contents of the Henze steamer are withdrawn at this temperature, when the diastase acts most powerfully and the greatest amount of sugar is formed. The mash is allowed to stand twenty to thirty minutes at this maximum saccharifying temperature, then the temperature is raised to 144° F. rapidly by running more of the hot mash with rapid stirring and cooling, and the temperature kept at this height for some little time. Here the maximum liquefaction of the starch takes place, while injurious germs are seriously weakened. Finally the rest of the mash is blown in rapidly and the temperature rapidly raised to 150°-154° F., when all undesirable germs are killed. The process of saccharisation is complete in less than one hour. The mashing is now completed so far as its first stage is concerned, and after cooling to the proper pitching temperature, will be ready for the addition of the yeast.

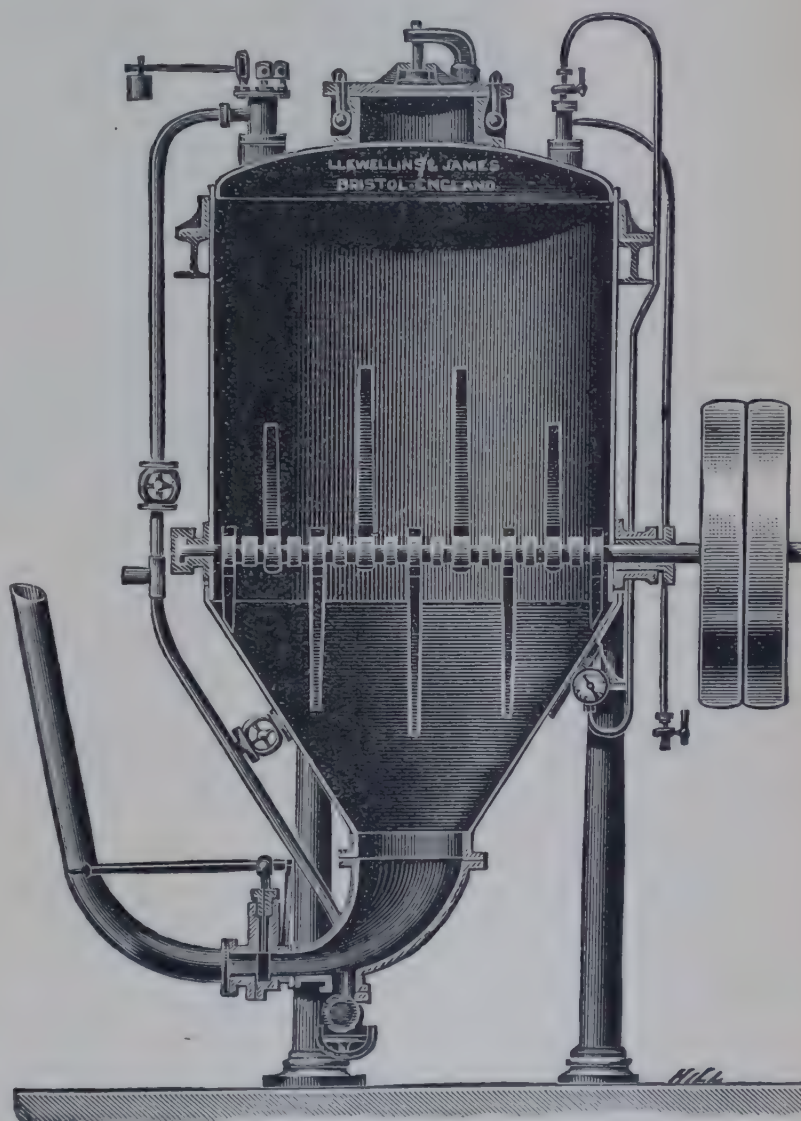


FIG. 123.—High-Pressure Converter for Raw Grain.



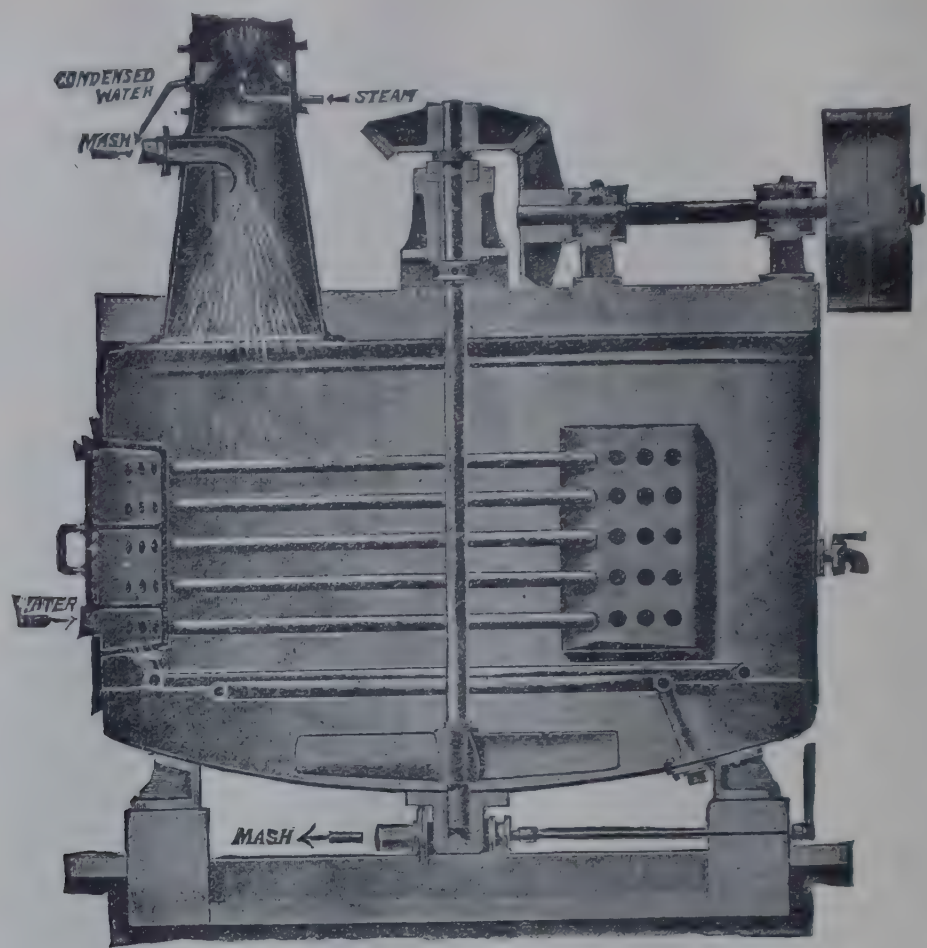


FIG. 124.—Centrifugal Mashing and Cooling Apparatus for Distilleries.  
(Gebrüder Sachsenberg, Rosslau in Anhalt, Germany.)

**Testing the Sweet Mash.**—Sugar solutions possess higher specific gravities than water. The greater the proportion of sugar present the greater the specific gravity, as the following table shows :—

BALLING'S TABLE OF THE SPECIFIC GRAVITIES OF SUGAR SOLUTIONS AT  
17.5° C. (63.5° F.)

Sugar in 100 Parts by Weight of Solution.	Specific Gravity.	Sugar in 100 Parts by Weight of Solution.	Specific Gravity.	Sugar in 100 Parts by Weight of Solution.	Specific Gravity.	Sugar in 100 Parts by Weight of Solution.	Specific Gravity.
0	1.0000	20	1.0832	40	1.1794	60	1.2900
1	1.0040	21	1.0877	41	1.1846	61	1.2959
2	1.0080	22	1.0922	42	1.1898	62	1.3019
3	1.0120	23	1.0967	43	1.1951	63	1.3079
4	1.0160	24	1.1013	44	1.2004	64	1.3139
5	1.0200	25	1.1059	45	1.2057	65	1.3199
6	1.0240	26	1.1106	46	1.2111	66	1.3260
7	1.0281	27	1.1153	47	1.2156	67	1.3321
8	1.0322	28	1.1200	48	1.2219	68	1.3383
9	1.0363	29	1.1247	49	1.2274	69	1.3445
10	1.0404	30	1.1295	50	1.2329	70	1.3507
11	1.0446	31	1.1343	51	1.2385	71	1.3570
12	1.0488	32	1.1391	52	1.2441	72	1.3633
13	1.0530	33	1.1440	53	1.2497	73	1.3696
14	1.0572	34	1.1490	54	1.2553	74	1.3760
15	1.0614	35	1.1540	55	1.2610	75-35	1.3824
16	1.0657	36	1.1590	56	1.2667		1.3847 =
17	1.0700	37	1.1641	57	1.2725		saturated
18	1.0744	38	1.1692	58	1.2783		sugar solution
19	1.0788	39	1.1743	59	1.2841		at 17.5° C.
							(63.5° F.)



Consequently, the determining of the specific gravity of the wort (by means of a hydrometer, called in this case a **saccharometer**) gives at once the approximate amount of sugar in the solution. Usually the percentage of sugar is directly marked off on the neck of the instrument, the values so obtained being known as "**degrees Balling**"—from the name of one of the introducers of the method into the distillery. In England and America **Bates'** saccharometer is largely used. The results are usually marked correct for a certain temperature (usually  $17.5^{\circ}\text{C.}$ , or  $63.5^{\circ}\text{F.}$ ), and the results for other temperatures are obtained by special tables.

Other tests applied to the sweet mash are:—

1. **Iodine solution** should produce no coloration. Any trace of starch present which has been unacted upon by the diastase would give a deep blue colour, and shows that the diastase is not working efficiently.

2. The presence of active diastase in the mash liquid, after the starch has been converted, is necessary for the after-fermentation. This is tested for by gelatinising 5 g. of starch with 200 c.c. water, cooling to  $144^{\circ}\text{F.}$  ( $62.3^{\circ}\text{C.}$ ), and adding 5 c.c. of mash liquid. The starch should be liquified almost instantaneously, and after thirty minutes iodine solution should not give a coloration with the liquid.

3. The acidity of mash is determined by titration with  $\text{NaOH}$ , so that the increase of acidity during fermentation may be known.

4. The amount of carbohydrates capable of fermentation is ascertained by inverting part of the filtered and diluted mash with  $\text{HCl}$ , neutralising, and estimating the sugars with Fehling's solution in the ordinary way.

**Process of Fermentation.**—Distillery yeasts work best at a temperature considerably above that most favourable to brewing types. If the distiller works at brewing temperatures brewing yeasts will predominate and these produce considerably less alcohol than proper distillery yeasts.  $75^{\circ}\text{--}81^{\circ}\text{F.}$  are temperatures favourable for distillery yeasts,  $60^{\circ}\text{F.}$  for beer yeasts, and  $40^{\circ}\text{F.}$  for wild yeasts.

Distillery conditions of fermentation are very favourable to the development of bacteria (since distillers work with unsterilised wort and at high temperatures) which lower both the yield and the quality of the alcohol. The most dangerous of these are the butyric, mannitic, and mucic bacteria. These are suppressed by fermenting in a "soured" or acid wort and working at a high temperature. The acid usually used is lactic acid, but hydrofluoric acid is coming into use. A slightly acid wort favours the development of distillery yeasts, but checks brewery yeasts and bacteria. The souring is not carried out with the main wort, but a small mash (English "bub," German *Hefegut*) specially mashed at  $148^{\circ}\text{--}158^{\circ}\text{F.}$  from kilned malt, to which is added unmalted wheat, maize, or rye. The potato mash itself has not enough yeast food for the vigorous propagation of yeast. This mash is heated to  $122^{\circ}\text{F.}$  ( $50^{\circ}\text{C.}$ ), and inoculated with a pure culture of lactic acid bacteria (sometimes the proper quantity of artificial lactic acid is added instead). At  $122^{\circ}\text{F.}$  they rapidly develop since no other bacteria appear capable of withstanding so well this high temperature in acid solution. When about 1 per cent. of lactic acid is present (determined by titration) the temperature is raised to  $165^{\circ}\text{F.}$  ( $73.9^{\circ}\text{C.}$ ) to kill the lactic acid bacteria and prevent souring proceeding in the main wort. The liquid is then cooled to  $80^{\circ}\text{F.}$  ( $26.7^{\circ}\text{C.}$ ), pitched with distillery yeast, cooled down very slowly with the attemperator to  $60^{\circ}\text{F.}$  ( $15.6^{\circ}\text{C.}$ ). The temperature then rises as fermentation proceeds, but must be kept under  $85^{\circ}\text{F.}$  Malt whisky distillers work at somewhat lower temperatures. Fermentation is forced as far as possible to convert all the sugar into alcohol.

Under these conditions practically only distillery yeasts thrive. Thus it has been shown that when a mixture of **brewery** and **distillery** yeasts have been applied three to four times to the sour wort, only pure distillery yeasts survive, the brewery yeasts having been killed.

Instead of lactic acid as the souring acid, a dilute solution of hydrofluoric acid has been used with great success, since the acid is poisonous to bacteria in an amount which does not affect distillery yeasts. Such yeasts can be acclimatised to stand 0.2 per cent. of the acid, a quantity which is quite fatal to any bacteria. Consequently, worts treated with hydrofluoric acid produce no side fermentation; while the acid, apparently, greatly stimulates the converting effect of the diastase, and thus permits low-mashing temperatures to be used.

The two distillery yeast races most widely employed and giving excellent results are **Species II.** and **XII.**, which have been produced by Lindner in the laboratories of the *Berlin Distillers' Association*. At the beginning of the season the



soured wort is pitched with the pure yeast culture, but as soon as this ripens and develops part is withdrawn and used as mother yeast for developing a fresh supply. Since in the distillery the danger of infection at high temperatures is very great it is necessary to frequently renew the supply of yeast.

Ten to fourteen hours after pitching the yeast has increased four to five fold, and the yeast is "ripe." When this occurs it is run into the main or "sweet" wort and the fermentation begun as rapidly as possible, for if the yeast do not rapidly develop foreign bacteria will make their appearance. The initial temperature is 68° F., but the temperature rises as fermentation proceeds. The chief period of fermentation occurs after twenty-four hours, decreasing again after twelve to eighteen hours. In this period of "after-fermentation" the diastase still present in the wort completes the conversion of any dextrine still present into maltose, which is then fermented by the yeast.

The temperature is kept during the whole fermentation under 86° (F. 30° C.) by means of a cooling coil (attemperator), for at higher temperature much alcohol is lost by evaporation and deleterious by-products are produced.

In Germany the worts are produced with as high a specific gravity as 1.110 ("Thick Mash") owing to the method of raising the duty, and a dilution of the mash with water towards the end of the fermentation acts very favourably by lowering the percentage of alcohol and CO<sub>2</sub>, thus stimulating the yeast to a fresh degree of activity. In malt whisky distilleries the specific gravity of the wort is 1.050-1.060, but in grain distilleries the worts approximate the German gravity.

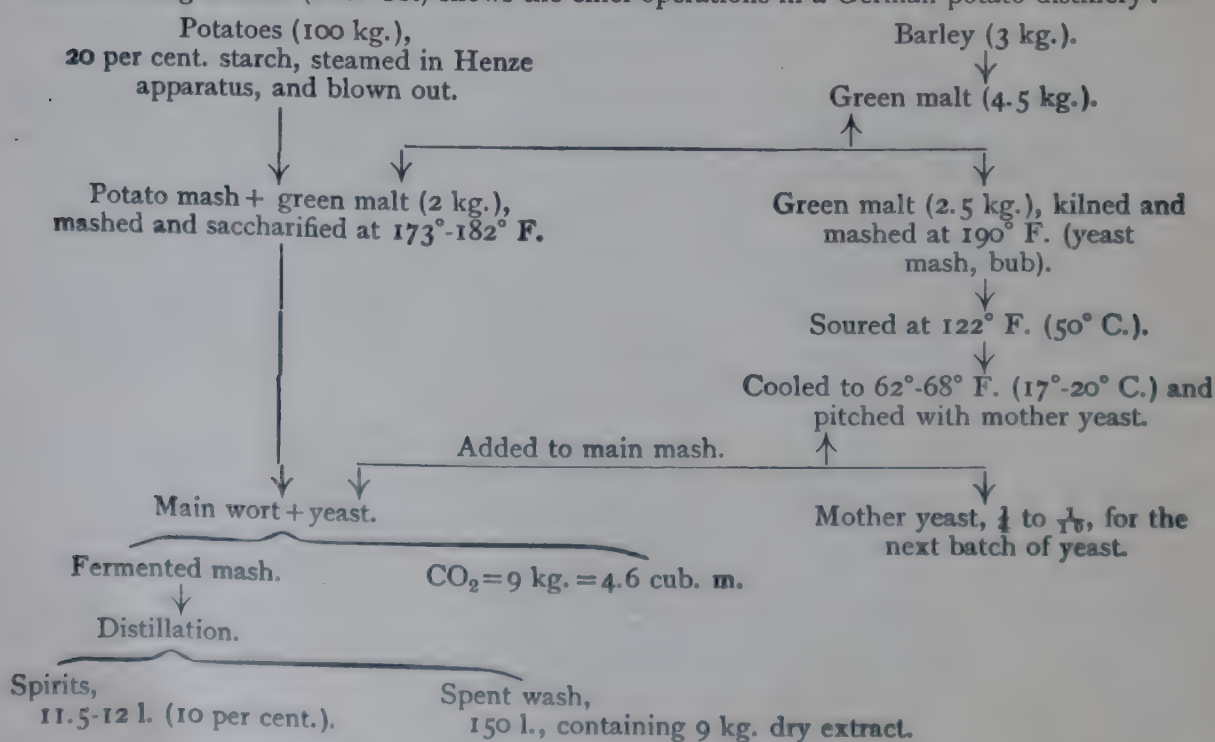
According to Maercker, concentrated mashes ferment more purely than thin mashes, and yield 12 or more per cent. of alcohol, which affords an excellent protection against injurious bacteria during fermentation. Moreover, they are more economical as regards time, cost, and work for producing a given amount of spirit than a thin mash.

In Germany the employment of thick potato mash is universal, because the mashing capacity is subject to taxation, and consequently the mashes are made as concentrated as possible in order to obtain the greatest possible yield of alcohol from the mashing capacity.

As a rule for thick mashes the fermenting vats have a capacity of 3,000-5,000 l. In the case of thin mashes and for molasses the fermenting vats have often a capacity of 40,000 l. Obviously the larger the vat the greater the amount of heat used for warming, etc., and for distilling the alcohol. It is usual to allow one-tenth of the fermenting vat clear for rising. Thick mashes in Germany contain 23-25 per cent. of sugar and dextrines. In corn distilleries the mashes contain 14-16 per cent. of sugar. In France and other countries where sugar beet and molasses are fermented the mashes often contain considerably less sugar than this.

In Germany the total time for fermenting is fixed by the custom officials at seventy-two hours.

The following scheme (after Ost) shows the chief operations in a German potato distillery:—



**Yield.**—As a rule about 2 per cent. of starch remains in the skins, etc., of the potato or corn. Of the dissolved starch about 5 per cent. remains unfermented.



Further losses also occur during fermentation owing to the production of by-products such as lactic acid, acetic acid, succinic acid, glycerol, fusel oils, yeast cells, etc. Also a perceptible loss of alcohol through evaporation occurs. Consequently, although according to the equation  $C_6H_{10}O_5 + H_2O = 2C_2H_5OH + 2CO_2$ , 100 parts of starch are capable of yielding 71.6 l. of alcohol, in practice only 58.60 l. are obtained. 100 kg. of starch yield 46 kg. of  $CO_2$  (= 24 cub. m.). This all escapes into the air as it is not economical to collect it.

### Alcohol from Beet and Cane Sugar Molasses

Beet sugar molasses is somewhat difficult to ferment, firstly because it contains only a small amount of nitrogen and phosphorus for yeast foods, and secondly because of the presence of fatty acids and bacteria, which prevent the yeast from developing.

The method usually adopted for working up these residues is as follows: The alkaline molasses is mixed with two to three times its weight of water, just acidified with  $H_2SO_4$  or  $HCl$ , and boiled in open vessels to sterilise the fluid and volatilise

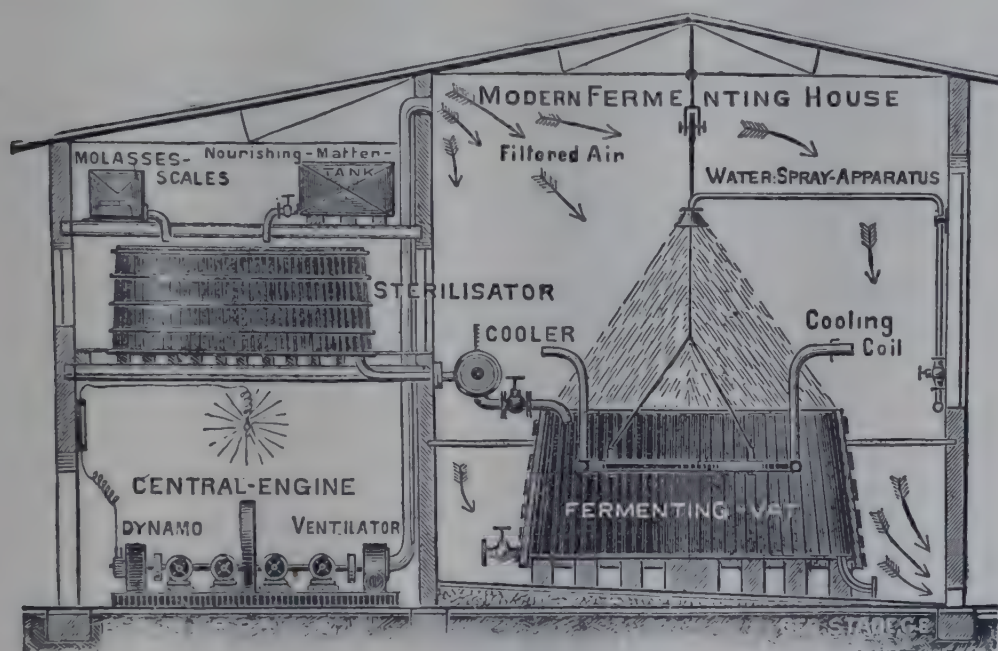


FIG. 125.—Fermenting Room of a Molasses Rum and Spirit Factory in Jamaica.

(Designed by George Stade, Berlin.)

some of the objectionable fatty acids, etc. The fluid now contains 15-17 per cent. of sugar, inverted by boiling with the acids and has sp. gr. 13° Bé. Solutions containing more sugar ferment badly. The mass is now cooled to 77° F. (25° C.), one-third is withdrawn and mixed with the yeast, and fermentation allowed to go on for some hours, when it is again returned to the main amount of molasses. The fermentation takes place quietly in large vats holding 200,000 to 400,000 l. and provided with cooling apparatus. The fermentation is usually incomplete, and a considerable amount of evil-smelling fusel oils are produced, but are separated from the crude spirit during the final distillation. Amine bases, formic acid, and aldehyde are present in crude molasses spirit.

Kraul & Wilkening confine their molasses in closed iron tanks of 400 hl. capacity, and cooled by a spray of water running over the exterior surface. This prevents the volatilisation of alcohol, and the  $CO_2$  escaping from the vessels is pumped off, purified, and compressed into cylinders. The yeast used is bottom-fermentation beer yeasts, and the yield is 25,000 l. of alcohol (100 per cent.) and 1,800 kg.  $CO_2$  per vat.

Geo. Stade of Berlin has effected several improvements in the manufacture of Jamaica rum from cane sugar molasses. A sketch of the fermenting room is shown. The rum ferment differs in structure from beer yeasts, having a maximum fermentative power at 30°-35° C. (86°-95° F.), is very sensitive to cold, and develops under special conditions into a mycelium.

The residues left after the fermentation of the molasses and distillation off of the alcohol are extraordinarily rich in **potash**, and contain nitrogen. The residues are evaporated dry, and used as manure, or they are worked up for potash, ammonia, and cyanogen compounds (see p. 376).

The calcined residues are known as calcinated vinasse (German *schlempekohle*), and contain 40-70 per cent. of potash salts. See under **Sugar**.

### Alcohol from Wood

The production of alcohol directly from wood in an economical manner is one of the great industrial problems of the present time. 55-60 per cent. of wood is composed of cellulose,  $(C_6H_{10}O_5)_n$  — a very complex carbohydrate — which, when treated with concentrated  $H_2SO_4$ , first dissolves to "amyloid," and then, after diluting with water until the solution contains 1-2 per cent. of acid, and heating to  $120^\circ C.$  under pressure, is readily transformed into dextrose,  $C_6H_{12}O_6$  — a fermentable sugar. In other processes, such as Simonsen's, the wood is directly heated with dilute  $H_2SO_4$  under a great pressure, when it is transformed into dextrose. The solution is then neutralised and fermented. The disadvantage of these latter methods is, however, that the dextrose formed is partially destroyed again at the high temperatures and pressures employed, and consequently the yield of alcohol from cellulose sinks to 15 per cent., or from wood alone (sawdust, containing 55-60 per cent. cellulose) only 5-6 per cent. alcohol. Starch under similar conditions gives a far more abundant yield, 100 kg. starch giving 60 l. of alcohol (48 per cent. yield). In the manufacture of sulphite cellulose for paper from wood, to every ton of cellulose treated, nearly 10 tons of sulphite wash results, containing over 1 per cent. of fermentable sugar. In Sweden efforts have recently been made to utilise this waste fluid by neutralising with  $CaCO_3$ , fermenting with yeast, and distilling for spirit. 1,000 volumes of the wash yields 6 volumes of alcohol (100 per cent.), which contains a considerable amount of methyl alcohol, and may be used as methylated spirits. See **W. P. Cohoe**, "Hydrolysis of Sawdust," *Journ. Soc. Chem. Ind.*, 1912, 513.

Willstätter and Zechmeister (*Ber.*, 1913, 46, 2401-2412) completely convert cellulose into dextrose at ordinary temperatures by treating it with a strong solution of HCl gas in water (40-41 per cent. HCl) for 24-48 hours, a very notable advance.

The distillation of the alcoholic liquors, in order to obtain pure alcohol, is treated at length in the following article by Mr W. H. Stephens.

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# DISTILLATION OF ALCOHOLIC MASHES AND MODERN DISTILLING PLANT

## LITERATURE RELATING TO DISTILLATION

Details of plant and methods used in distillation are given in the numerous works on spirits and industrial alcohol mentioned in the section on **Spirits** and industrial alcohol, p. 278. The following works specially deal with distillation and may be recommended:—

BARBET.—“La Rectification.” Paris, 1895.

SOREL.—“La Distillation.” Paris, 1898.

„ “La Rectification de l’Alcool.” Paris, 1894.

HAUSBRAND.—“Die Wirkungsweise der Rectificier- und Destillir-Apparate.” Berlin, 1893.

The most concentrated alcoholic mashes contain only 10-12 per cent. of alcohol, and to separate the alcohol in a concentrated form from the mash recourse must be had to distillation. Pure absolute alcohol boils at  $78.3^{\circ}$  C. (760 mm.), whereas water boils at  $100^{\circ}$  C.

**Simple Distillation.**—Certain classes of alcoholic beverages, *e.g.*, whisky, brandy, rum, etc., depend for their characteristic flavours on the retention of a considerable amount of volatile by-products of the wash. For this kind of product the simple stills are the best, since they do not effect the complete separation of the alcohol and the fusel oils, the presence of the latter being essential for giving a characteristic odour to the beverage. Such beverages contain 25-60 per cent. of alcohol.

Fig. 126 shows a simple still for brandy—A is the body of the still, c the head, and s the condensing worm, which is immersed in a tank of water. The spirit runs out through x and is received in a suitable receptacle.

The pot stills of Scotch and Irish whisky manufactories are of this type, although larger, and usually set in masonry over a naked fire. Sometimes the stills are heated

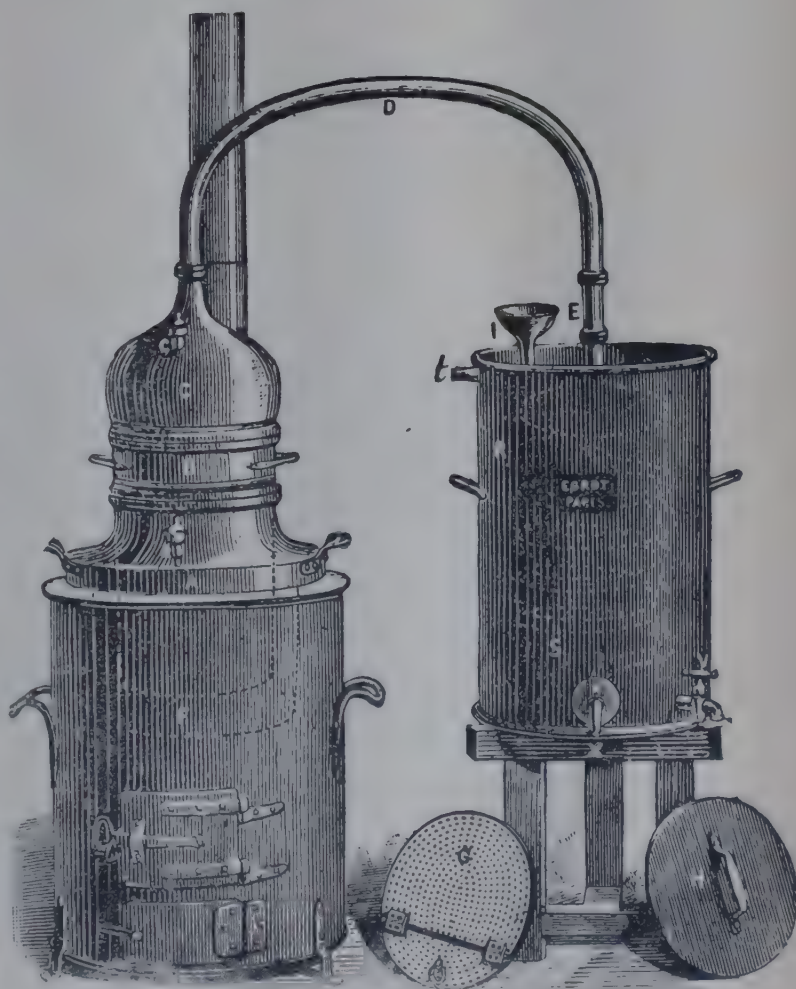


FIG. 126.—Simple Still for Brandy.  
(Egrot, Paris.)

by steam jackets or steam pipes. The neck of the still is long; the rectifying effect

thus obtained is sometimes enhanced by the introduction of rectifying devices between the still and the condenser. The first distillate is richest in alcohol. When one-third to one-half of the wash has been distilled over the residue is "spent wash" free from alcohol. The distillate contains much water, and to raise the alcohol content it must be repeatedly distilled.

The following numbers suffice to give an idea of the results obtained with a simple still of this kind: 1,000 volumes of mash containing 10 per cent. of alcohol were distilled until 400 volumes passed over, this 400 volumes was again distilled and so on. The alcohol percentages in the resulting distillates is shown below:—

(1)	1,000	volumes	when	distilled	yielded	400	volumes	liquid	containing	25	per	cent.	of	alcohol.
(2)	400	"	"	"	"	200	"	"	"	50	"	"	"	"
(3)	200	"	"	"	"	140	"	"	"	71	"	"	"	"
(4)	140	"	"	"	"	125	"	"	"	80	"	"	"	"

Four separate distillations, therefore, were required to give a product containing 80 per cent. of alcohol and by repeated distillation it is possible to obtain a spirit of 96-97 per cent. alcohol. Further it is impossible to go; the remaining 3-4 per cent. of water must be withdrawn by dehydrating chemicals, such as lime or potash.

In making Scotch whisky two distillations are resorted to, the wash being distilled to yield a "low wine," which is again distilled. The final distillation is divided into three fractions: (1) foreshots, (2) finished whisky, (3) feints. The foreshots and feints comprise the various secondary products together with alcohol and added to the low wines for re-distillation. The less volatile portions of these by-products finally pass away with the spent wash.

Irish whisky is generally obtained by a process involving three distillations, in which a more complex classification of the products is effected, *e.g.*, strong and weak low wines, and strong and weak feints are often separated.

In both Scotch and Irish stills, soap is often added to the charge in the wash still to prevent frothing, and charcoal is added to the low wine still for purifying purposes.

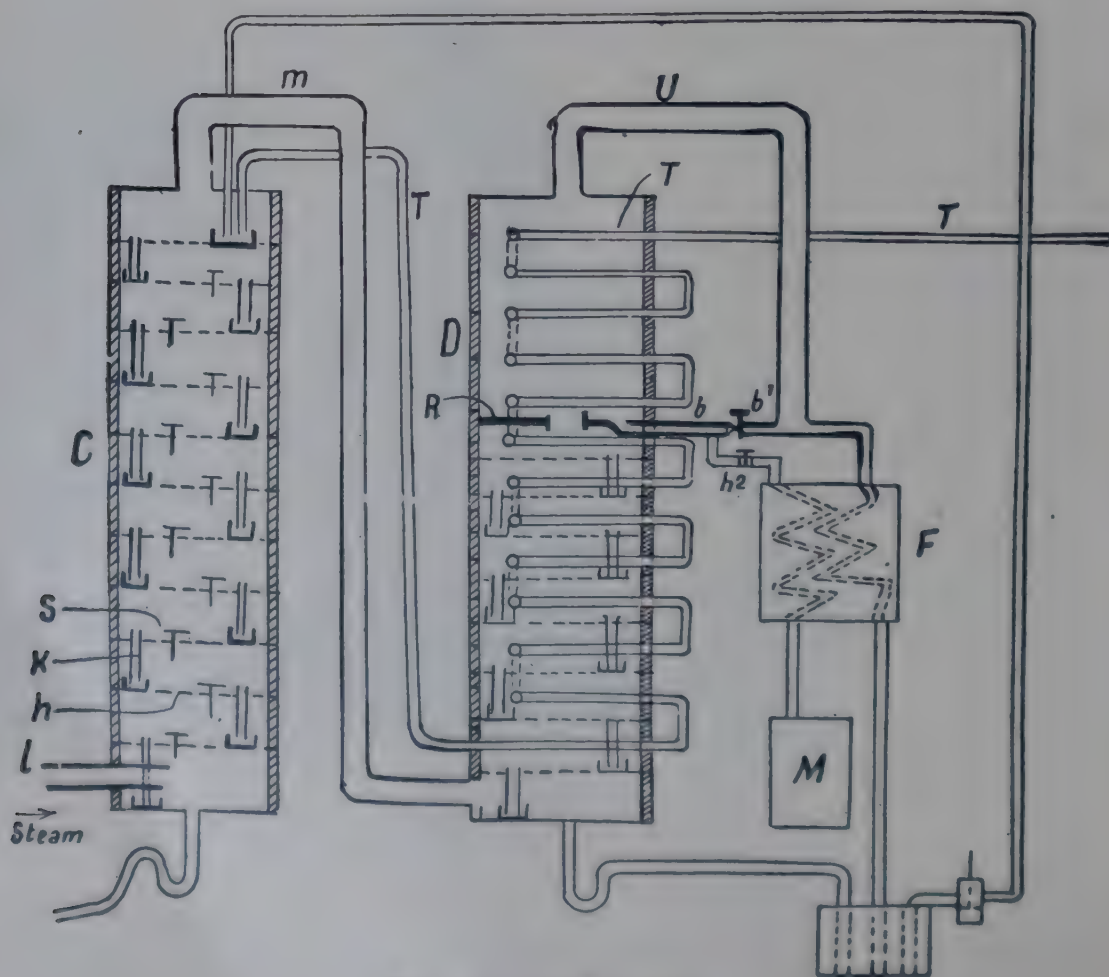


FIG. 127.—Coffey's Still.



**Continuous Distillation.**—The simple stills previously described do not remove the by-products except after repeated redistillations, and moreover the method of operation is discontinuous. Very early in the last century efforts were made to construct continuous stills which gave in a single operation a more concentrated spirit, and which removed to a great extent objectionable by-products. A still

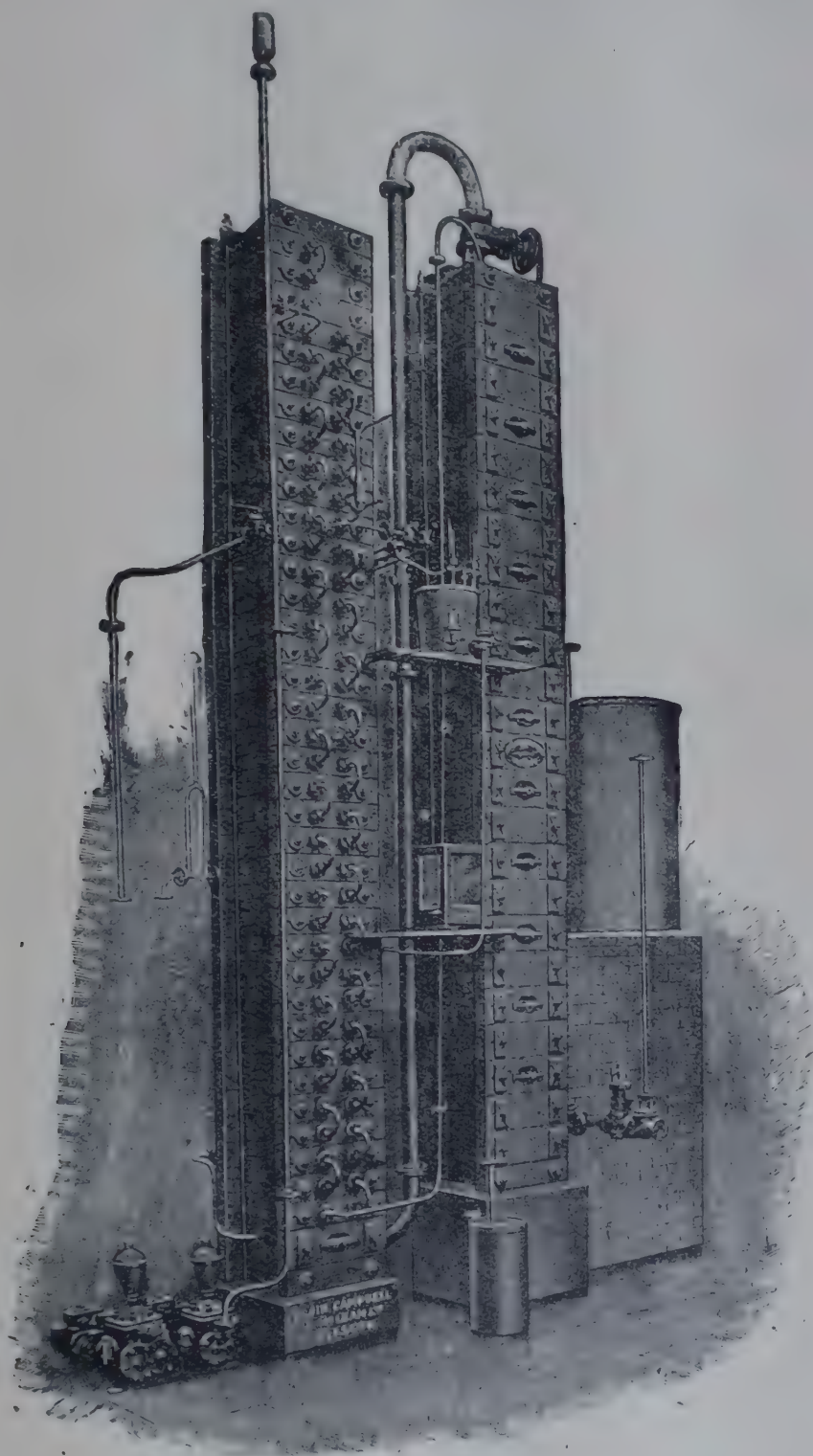


FIG. 127a.—Blair, Campbell, and M'Lean's form of Coffey's Still.

which has been largely used, and is still largely used, by British and Irish distillers, is the apparatus invented by Æneas Coffey in 1831, and shown in Figs. 127 and 127a.

This still comprises two columns, the analyser *c* and the rectifier *d*, which are divided into chambers made of wood and braced together in an iron frame. The chambers are separated by copper plates *h*, each having a large number of small perforations. Each plate has a safety-valve *s* and a drop pipe *k* standing with its upper end 1 in. above the plate and dipping into a cup



on the plate below. These overflows *h* are so arranged that the liquid flows across each plate, pursuing a zigzag course through the column.

In operation, steam is passed into the analyser *C* by a pipe *l* and passes from the top of the analyser to the base of the rectifier *D* by a pipe *m*. When the columns are filled with steam, the wash is pumped through a coil of piping *T* entering the top of the rectifier *D* and passing through each compartment in succession to the bottom (the wash being thus heated, and the surrounding vapours cooled) and is discharged on to the top plate of the analyser *C*. The wash, heated almost to boiling, now flows down the column *C* in the face of an ascending stream of steam. The small holes in the plate *h* are large enough to allow the passage of steam up through them, but too small to allow the wash (in the face of the ascending current of steam) to pass through. The wash, therefore, can only pour down from one plate to another through the down-tubes *k*. Consequently the downcoming wash meets an ascending current of steam, which, bubbling through each layer of liquid on the plates *h*, deprives it of its alcoholic contents. The alcoholic vapours and steam are led away from the top of the analyser *C* to the base of the rectifier *D* by means of the pipe *m*.

Here a partial condensation of the vapours is effected by means of the coil *T* through which the wash is flowing. The vapours bubble through the reflux liquid thus provided in precisely the same manner as in the analyser *C*. As the vapours pass upwards, they become richer in alcohol; as the liquid flows downward, it becomes weaker in alcohol, though retaining the less volatile constituent, namely, the fusel oils.

At a particular part of the rectifier, where the temperature corresponds with the temperature of condensation of strong alcohol, is fitted a stout unperforated copper plate *R* (known as the "spirit plate" or "dumb plate"), pierced by a wide pipe which stands up about 2 in. above the plate. A two-branched pipe *b* drains this plate. Normally alcohol condenses above this plate and runs through one branch *b*<sup>2</sup> to the refrigerator *F* and thence to the "finished distillate" receiver *M*.

At the beginning and the end of the distillation (which normally lasts two or three days without intermission) weak spirit condenses, and is run through the other branch *b*<sup>1</sup> to the refrigerator and thence to the "hot feints" receiver below. The liquid (containing alcohol and fusel oils) flowing away from the base of the rectifier also passes to the "hot feints" receiver, and is pumped thence continuously throughout the distillation to the top of the analyser, and is there re-distilled. The weak spirit vapours escaping by a pipe *U*, together with the more volatile impurities from the top of the rectifier, are condensed and also led to the "hot feints" receiver. At the end of each period the fusel oils are removed from the "hot feints" receiver.

W. E. Bell gives the following analysis of a sample of fusel oils so obtained :—

Amyl alcohol	-	-	-	-	-	42.2 per cent.
Butyl "	-	-	-	-	-	33.4 "
Propyl "	-	-	-	-	-	18.9 "
Ethyl "	-	-	-	-	-	5.5 "

Ethyl esters of palmitic and oleic acids are also found in the "hot feints."

Fig. 127*a* shows a modern form of Coffey's still, as manufactured by Blair, Campbell, & M'Lean, of Glasgow.

Coffey's still has been described in great detail, not merely because it is the type in most common use in this country, but also because it affords a very valuable insight into the principles of continuous working. All continuous distilling plants comprise a continuous still, such as Coffey's analyser, and a continuous rectifier. Both the still and the rectifier are based on the same principle, namely, that by the repeated distillation and condensation that occurs in an apparatus in which a liquid and a vapour are flowing in opposite directions in intimate contact, the liquid is successively deprived of portions of its most volatile ingredients, and at the same time the vapour is successively deprived of portions of its least volatile ingredients, these being condensed and joining the down-flowing liquid, while the volatilised portions of the liquid pass on with the vapour. In the still, then, the wash enters at the top and meets a current of steam from below; the spent wash containing all the non-volatile ingredients and the major portion of the water passes out at the base, while the alcohol and volatile impurities together with water pass away at the top. In the rectifier, the vapours from the still enter at the base, while liquid provided by "dephlegmation," that is to say, condensation, flows downwardly; at the base, a liquid, comprising the major portion of the water together with fusel oils and small quantities of alcohol, flows away, while at the top the alcohol and the more volatile impurities (aldehydes, etc.) collect in the form of vapour and may be condensed.

These principles will be easily recognised as underlying the continuously working distilling plants in use on the Continent.

The type most widely used is that designed by Savalle. Fig. 128 shows a typical Continental still of this kind :—



A is the distilling column, B the rectifier, C the dephlegmator (or condenser) and preheater for the wash, D the alcohol condenser, G the alcohol outlet, E the spent wash outlet.

The mash is forced through the pipe *s* into the dephlegmator C, wherein it is heated; then it passes in a hot condition through the pipe *s*<sub>1</sub> into the uppermost chamber of the distilling column A. The spent wash flows away through a regulator E. Steam enters by a perforated pipe *b* and

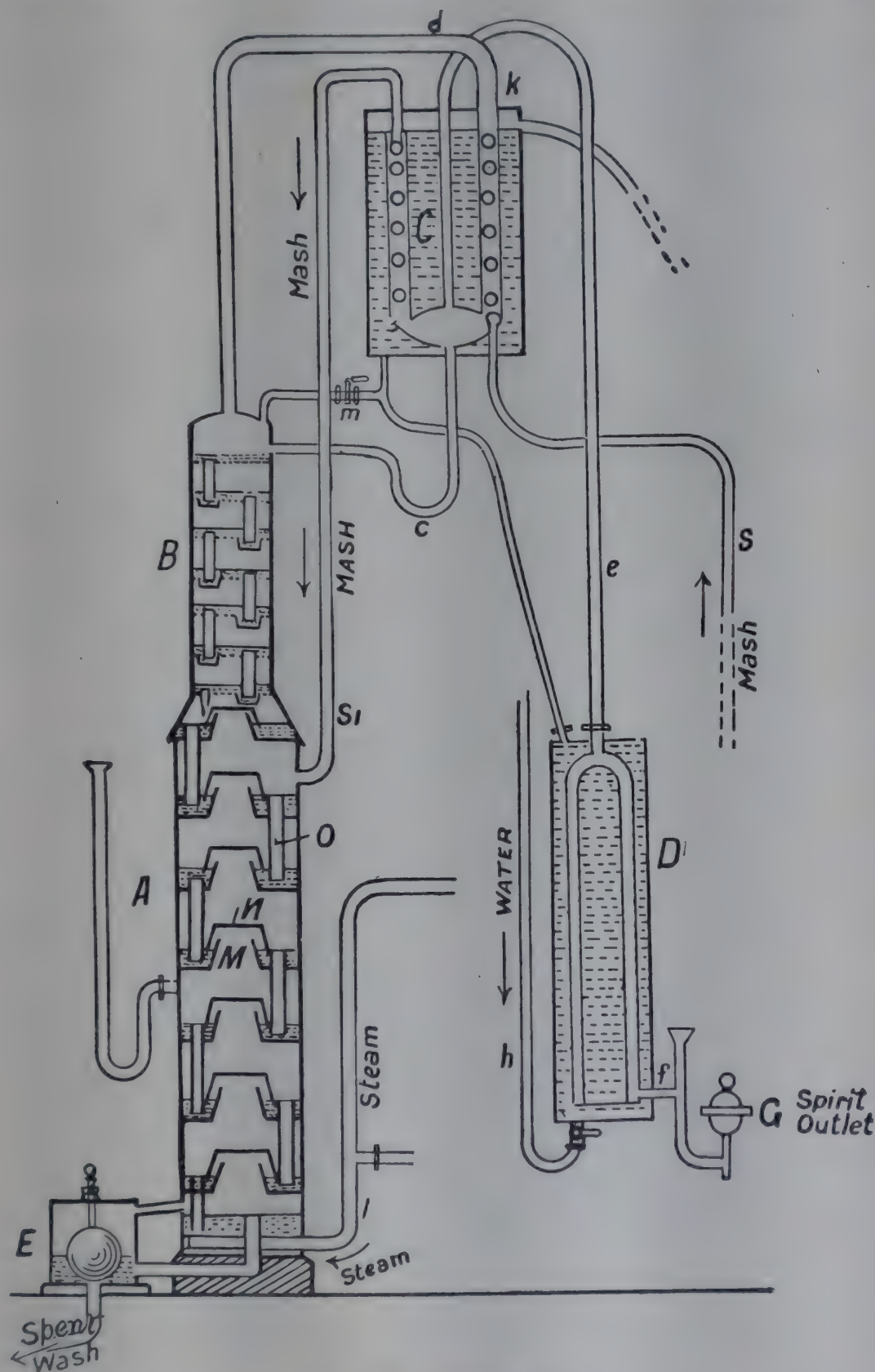


FIG. 128.—Savalle's Still.

vaporises the alcohol in the still A. The vapours enter the rectifier and pass away from the top by a pipe *d* to the dephlegmator C. The portions here condensed return by a pipe *c* to the rectifier. The remainder pass on to the spirit condenser by way of a pipe *e*.

The rectifying column B is composed of perforated plates of the same construction as Coffey's apparatus. The distilling column A is, however, of a different construction, and comprises plates

with central openings M surmounted by bells or hoods N, the lower edges of which dip below the surface of the liquid on the plates, which are provided with the usual overflow pipes O. The up-flowing vapours are thus caused to bubble through the liquid around the edges of the bells N (Fig. 128 and 129).

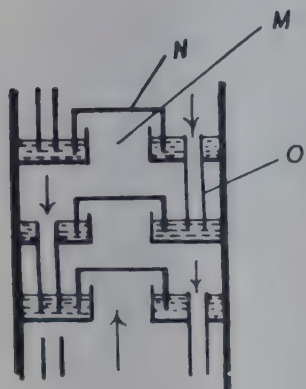
The dephlegmator shown consists of a tank filled with water. It contains a double-walled, annular vessel, through which the vapours pass, and which in its turn surrounds a copper worm through which the mash from the fermenting vat is pumped.

The main point in which this plant differs from Coffey's apparatus is that the dephlegmator and preheater for the wash C is entirely separated from the rectifier, no temperature exchange between the vapour undergoing rectification and the wash to be distilled being effected in the rectifier. It is the vapour from the top of the rectifier which exchanges heat with the wash, is thereby condensed, and returns by a pipe *c* to provide a reflux liquid in the rectifier. The column B is then a rectifier pure and simple. By this arrangement is obtained the advantage that the liquid which leaves the base of the rectifier must have been subjected to redistillation on all the stages of the column, whereas in the Coffey still some of the outflowing liquid may be derived from condensation in the lower part of the rectifier, and in consequence may not be satisfactorily freed from alcohol by redistillation.

A British still of this type is "Blair's" patent continuous steam working still, manufactured by Blair, Campbell, & M'Lean, Glasgow (Fig. 130).

It is obvious that the rectifying and distilling columns may be arranged side by side in the same manner as in Coffey's still. This arrangement has the advantage that the fusel oils may to a large extent be isolated and prevented from entering the distilling column. In modern plants for making industrial alcohol, it is not customary to pass the residue directly from the rectifier into the analyser in the manner described in connection with Coffey's apparatus.

The oils are usually allowed to separate from this liquor, and are decanted off continuously, the liquid from which the oils have been removed being returned to the distilling column. Plants embodying this operation are described on pp. 306-311, under **Continuous Rectifying Apparatus and Combined Distillation Rectification Stills**.



SECTION OF  
— TRAYS —

FIG. 129.

**Rectification.** — The various forms of distilling plant previously described do not provide alcohol sufficiently pure for industrial purposes. The raw spirit or phlegm contains a quantity of aldehyde and fusel oils. The operation of rectification is designed for the removal of these substances. In the older type of rectifying plant, as introduced by Savalle, for example, the spirit after dilution with 40-50 per cent. of water is rectified in a still consisting of a large iron boiler A (Fig. 2, p. 6) heated by

steam, surmounted by a copper rectifying column B, 45 ft. often high, together with a dephlegmator C, from which liquid is returned to the rectifier by a pipe *m*, and a spirit condenser D. The operation is discontinuous, the boiler being filled with the diluted spirit and carefully distilled. The operation is then broken and the residues removed; then the boiler is refilled, and the distillation repeated. The loss amounts to 1.5-2 per cent. of alcohol.

The raw spirit was thus separated into four products, viz.: (1) **First runnings or foreshots**, which is a mixture of acetaldehyde and ethyl alcohol. It boils at a lower temperature than pure ethyl alcohol, and is called **ether** by the refiner. (2) **Clean or rectified spirit**, which is the intermediate product, and consists of almost pure alcohol, 96-97 volumes per cent. (3) **Feints**, a mixture of various alcohols, consisting of some ethyl alcohol and much amyl alcohol, and similar alcohols of high boiling points. (4) **Fusel oil**, which remains in the still together with the water.

**Charcoal Filters.** — The alcohol as it came from Coffey's and older stills contained anything between 80 and 90 per cent. of alcohol by volume, and always had a certain amount of fusel oil and aldehyde in it. These must be removed before the alcohol is fit for adding to good wines, liqueurs, etc., or can be used for many chemical purposes. It was therefore the custom to filter it through charcoal filters, which greatly improved its quality. Owing to the presence of absorbed oxygen in its pores the charcoal acts chemically on the higher alcohols, oxidising them to acids (also to



aldehydes), which then form esters with the excess of alcohol. Part of these esters are retained by the charcoal, but some remain in the spirit; consequently, although filtration through alcohol improves the taste and smell of the alcohol, it does not completely remove all the fusel oil. The charcoal, broken into lumps, is placed in a number of iron cylinders (which are sometimes 30 ft. high) arranged in series, and the spirit, after diluting to 50 per cent., is allowed to slowly flow

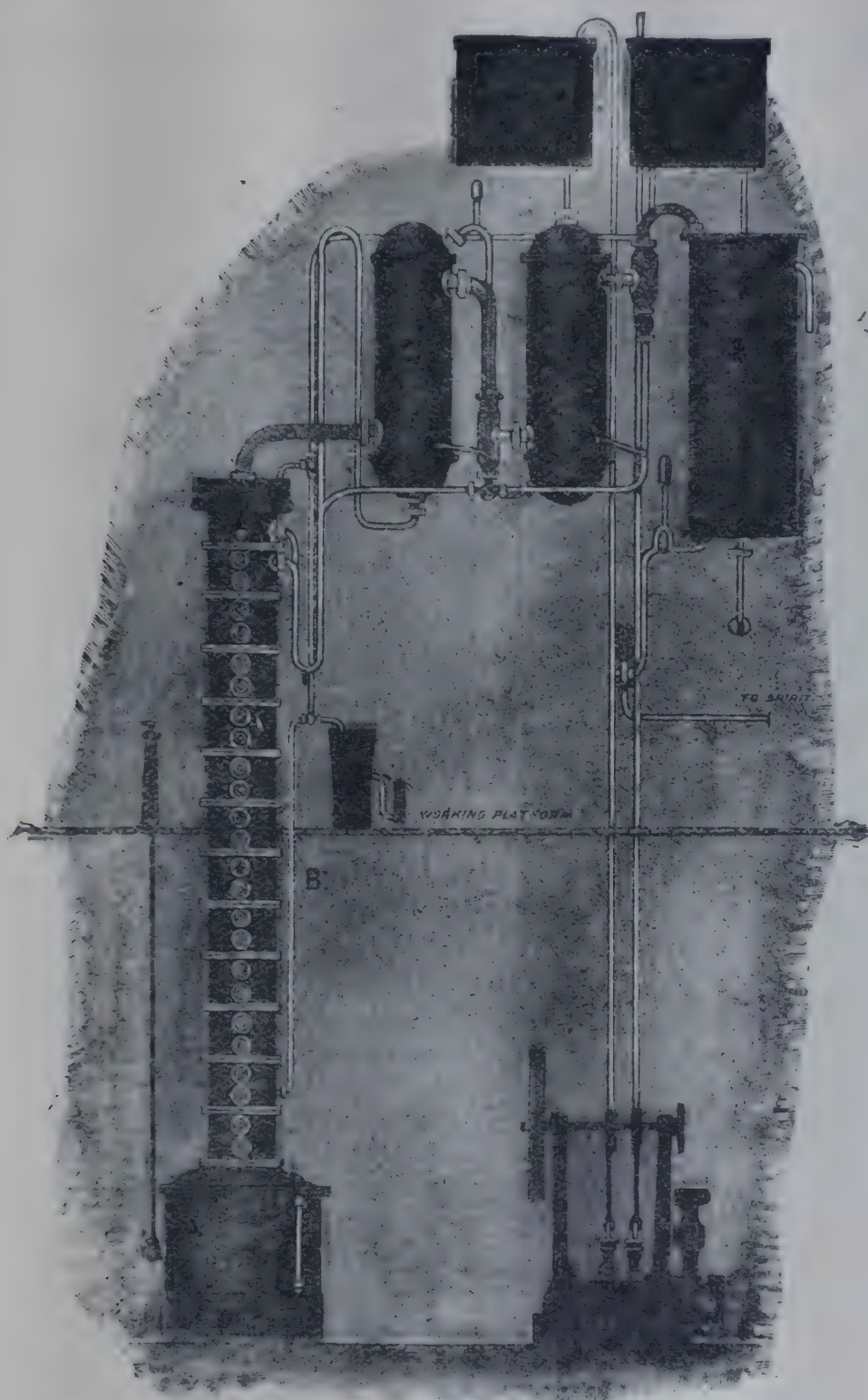


FIG. 130.—“Blair’s” Patent Continuous Working Steam Still.

A, Still Kettle with Steam Coils; B, Analysing and Rectifying Column;  
C, D, Rectifying Wash Heaters; E, Condenser.

through them (Fig. 131). The last traces of alcohol are recovered by blowing steam through the charcoal, and it is regenerated by heating to redness in special furnaces.

Within recent years the expensive process of filtering through charcoal has been largely dispensed with, the distillers relying on carefully conducted rectification for the complete removal of the fusel oil and acetaldehyde, the former being now a valuable by-product (see pp. 312 and 383).



Before proceeding to a detailed description of more modern types of plant (including continuous apparatus for rectifying alcohol) it may be as well to note the different forms the various integers of the apparatus already described may take, and the additional devices which are essential to the efficiency of the apparatus.

**Distilling and Rectifying Columns.**—These are identical in principle, but since in the distilling column the distiller may have to deal with thick mashes which tend to block the various passages of the still, greater variation will be found

in the forms of apparatus adopted. The forms in most common use are those in which the vapours bubble through the liquid, and these again are divisible into (1) "Plate" columns; (2) "Full" columns. Types in which the liquid is brought into contact with the vapours in the form of films or spray are also known.

**Plate columns** are either of type described in connection with the Coffey still, comprising perforated plates, or of the type described in connection with the Savalle still, comprising large orifice surmounted by hoods by means of which the vapours are forced to bubble through the liquid (Figs. 128, 129).

An example of the form which a modern bubbling-hood plate takes is that used in Egrot's system, and shown in Fig. 132. This comprises a number of bells *k* arranged on a plate sloping towards the centre and provided with a number of partitions which force the liquid entering at *a* to follow a path *bcdefg* which brings it past each of the bells before it reaches the exit *o*. In both types of plate columns we get, in each compartment, a layer of liquid and above it a stratum of vapour.

**Guillaume's "inclined column"** (Fig. 133) closely resembles the "plate" type, and was devised to meet the problem of thick mashes. It has, however, proved useful as a rectifying apparatus. This apparatus is made in two parts; the upper part of the casing is provided with depending partitions 3 extending across the whole width of the column, while the lower part is furnished with upstanding partitions *d*, alternately stopping short of

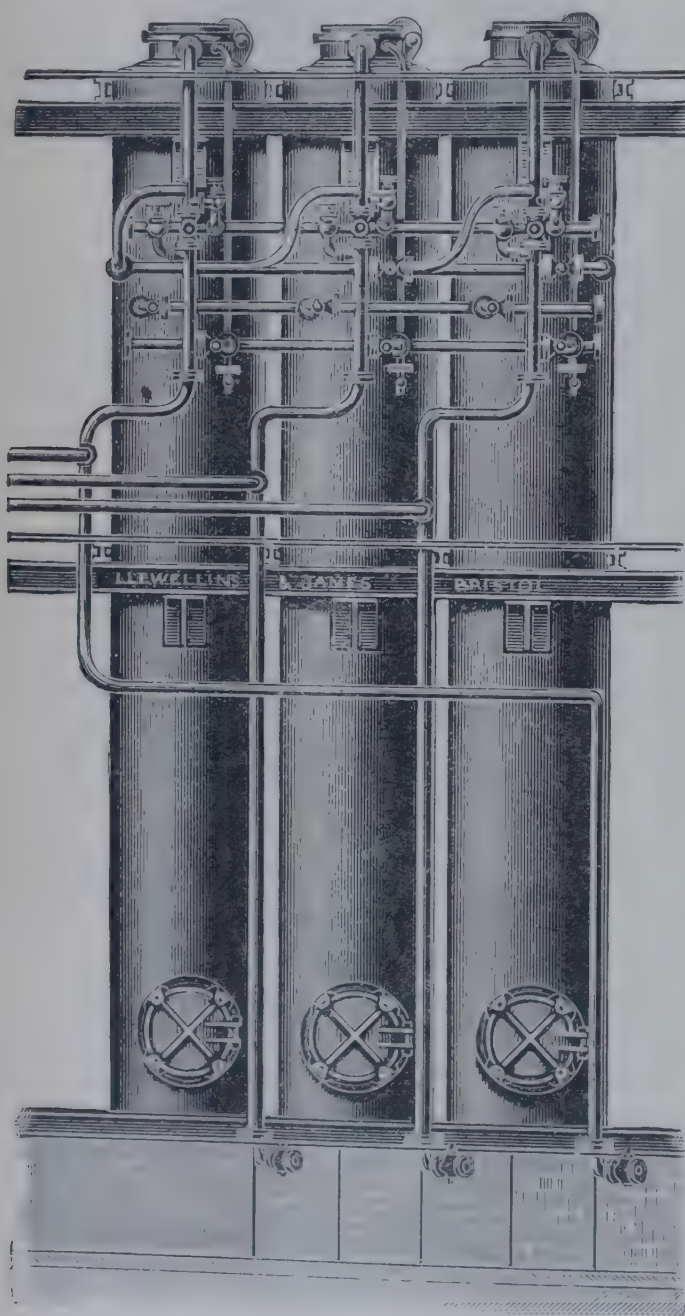


FIG. 131.—Charcoal Filters.  
(Llewellyn & James, Bristol.)

either side of the casing. The liquid thus follows a zigzag course from top to bottom, as indicated by the arrows, while the vapours are forced to bubble under each of the partitions 3.

**"Full" columns** are, however, full of mash, the vapours passing from bottom to top continuously in bubble form. Obstructions cannot arise in this type of column, but unfortunately it is much less efficient than the "plate" type, and is therefore never used for rectifying purposes. The still used by Ilges, and shown in Fig. 134, is a good example of this type. It will be seen that the only internal fittings take the form of baffle plates *a*, *g*, which both lengthen and regularise the upward path of the vapours through the down-flowing liquid.

**Of Film types** two are worthy of mention, namely, those devised by Savalle and by Ilges.



**Savalle's** horizontal apparatus was devised primarily for dealing with thick mashes, and comprises a horizontal cylinder in which a number of discs partially immersed in liquid rotate on a horizontal shaft. The liquid flowing in one direction is thus continuously exposed in thin films to the action of the vapours flowing in the opposite direction. It is described in detail in British Patent 21,708, 1891.

**Ilges** and other inventors use a tower packed with glass balls or the like for rectifying purposes.

**Spraying** columns for distilling purposes have been devised by **Guillaume**; these are described in detail in British Patents, 3,561, 1903, and 11,475, 1906.

**Dephlegmators.**—A form of dephlegmator has been described on p. 300 in connection with Savalle's still. At one time it was thought that a dephlegmator such as that described had the effect of condensing from the vapours entering it a fraction containing the less volatile constituents, while allowing the more volatile constituents to pass on to the spirit condenser. According to this theory the dephlegmator thus had a rectifying or fractionating action. It cannot, however, be too strongly emphasised that the dephlegmators in common use, constructed as they are with cooling surfaces only, have practically no rectifying action, or, to use the words of Barbet, the condensed liquid has practically the same chemical composition as the mixture of vapours from which it is derived.

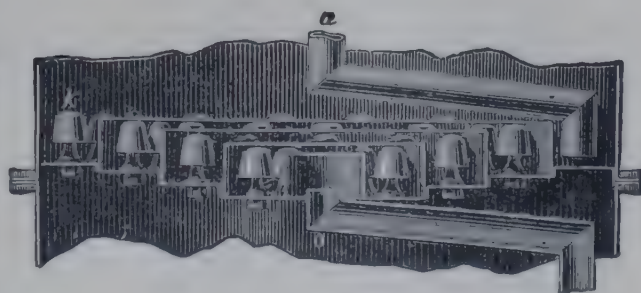
In France this principle has been largely recognised, and the evolution of distilling rectifying plant has followed lines entirely different from those based on the older theory.

Numbers of inventors—Ilges, for example, in Germany—working on the old theory and recognising that the dephlegmators in use were, from that point of view, highly inefficient, have improved their dephlegmators by combining with them constructions having a true rectifying action.

An example of such a type of dephlegmator is sketched in Fig. 135, which was designed by J. Verchow, Germany, and is constructed by Schmidt & Son, Nauen, Mecklenburg, Germany. It consists of three casings placed one within the other; the middle casing on both its inner and outer sides, and the inner casing on its outer side only, are provided with annular angle flanges riveted in position. The mash is pumped into the apparatus through A, and flows in a gradual spiral path formed between the outer and middle casing by the flanges, until it reaches the outlet B, whence it pours into the mash or distilling column. The alcohol vapours from the distilling column enter the dephlegmator at C and pursue a spiral course upwards through the space G between the flanges upon the outer side of the inner casing and the inner side of the middle casing, a large portion condensing on the way and flowing down the spiral into the distilling head by G, the rest passing on and partially condensing in the cooling chamber situated in the upper part of the dephlegmator, whereas the uncondensed alcohol vapour passes out through D into a condenser where it is condensed and drawn off as pure alcohol. The alcoholic vapours condensing in the upper cooling chamber run through the tube CC and trickle down between the flanged castings into the upper part of the distilling column. The inner casing is filled with cooling water which completely surrounds the cooling chamber. The mash is heated by the warm outer wall of the middle casing and in its turn cools the alcohol vapours.



Plan.



Elevation.

FIG. 132.—Egrot's Tray. (Egrot, Paris.)



It is by the introduction of these flanged castings, which provide a long path in which the liquid is to some extent removed from the cooling action of the walls and is subjected to the action of the hot vapours, that the repeated redistillations which constitute the operation of rectification are alone rendered possible.

The Wagener type of dephlegmator is based on the same principle. Here will be seen cooling and condensing surfaces constituted by corrugated walls *d* and tubes *a*, Fig. 135. These have no rectifying action. These surfaces are, however, provided with metal strips *i* and *c*, which enable the vaporisation of the liquid by the hot vapours, and which perform the actual rectification.

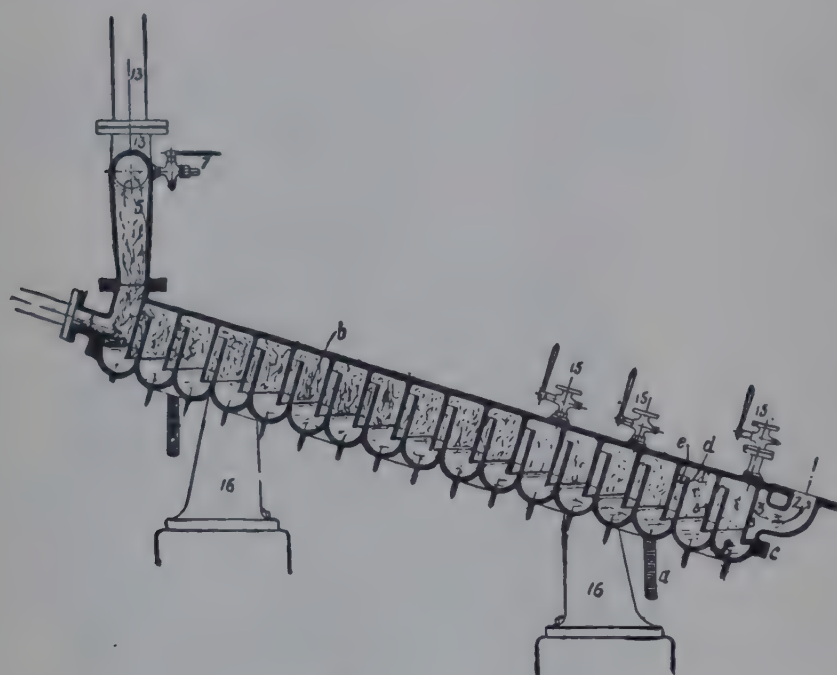
Apparatus fitted with dephlegmators, such as those described, yield with ease an alcohol of strength 89-92 per cent. by volume in place of the spirit of 80-87 per cent. strength obtained in plant not fitted with such apparatus.

### Pasteurisation.—

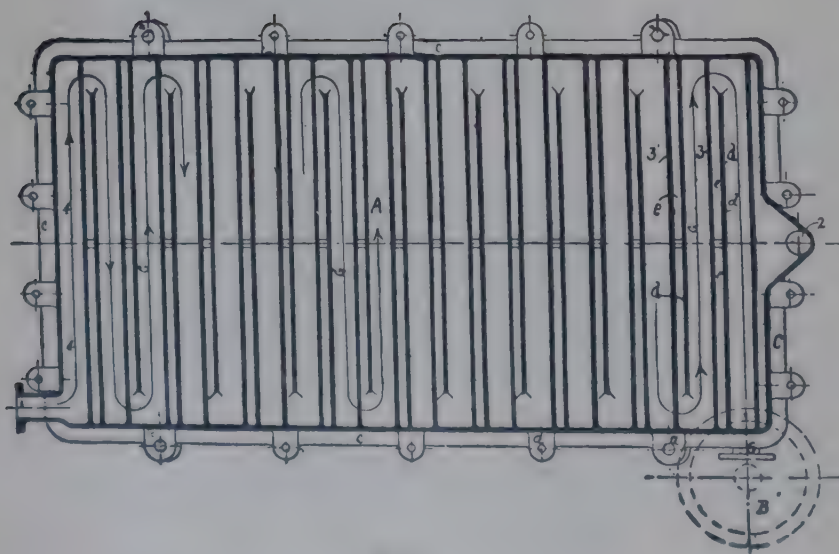
This operation is characteristic of the rectifying plant adopted in France. It is based on two principles:—

(1) A condenser as such has no rectifying action; that part of the vapours which is liquefied is of almost exactly the same composition as the part which is not liquefied, particularly when the alcoholic vapours are of high degree.

(2) If any plate of a column is charged with boiling liquid, and a vapour of the same temperature is made to bubble through that liquid, then of that vapour the portions which are more volatile than any portion of the liquid will pass on without being liquefied. The only change in the composition of the liquid and vapour which can take place is such that the vapour yields a portion of its less volatile



Elevation.



Plan.

FIG. 133.—Guillaume's "Inclined" Column.

constituents to the liquid, and the liquid yields a portion of its more volatile constituents to the vapour. Turning to Fig. 136 which shows the top of a rectifying column *A* surmounted by a condenser or dephlegmator *E* from which the condensed liquid is returned to the top plate *B* of the rectifier, we find that in conformity with the first mentioned principle that the liquid thus returned is of the same composition as the vapours entering the condenser *E*, and accordingly contains alcohol together with head-products (aldehydes and ethers) but that, in conformity with the second-mentioned principle, by the time that liquid has reached the third



plate of the rectifier, those head-products have been volatilised, and that accordingly pure liquid alcohol may be withdrawn from that plate through a pipe *H*. This operation is that known as "Pasteurisation," and the resulting product is "pasteurised" alcohol. The vapours that escape condensation in the dephlegmator *E* pass to a condenser *F*, are there condensed to yield a liquid containing head-products which are subjected to further treatment.

**Regulation.** — To obtain absolutely uniform products, it is necessary to ensure that the amounts of the various distillates and of the residues leaving the base of the columns per unit time are constant and correspond exactly with the amount of free liquid entering the apparatus, and further, that the temperatures and the quantity of liquid in any part of the apparatus are also constant.

For example, the amount of steam admitted for heating purposes is controlled by a thermostatic device which responds instantly to any variation of the temperature in the distilling column.

While it is not intended to describe in detail the various devices used to ensure uniformity of working, it may be as well to consider the arrangements used in conjunction with the pasteurisation apparatus previously described with reference to Fig. 136. These will afford an insight into the scrupulous care that is necessary to obtain satisfactory results.

It will be remembered that the vapours pass from the rectifier *A* through

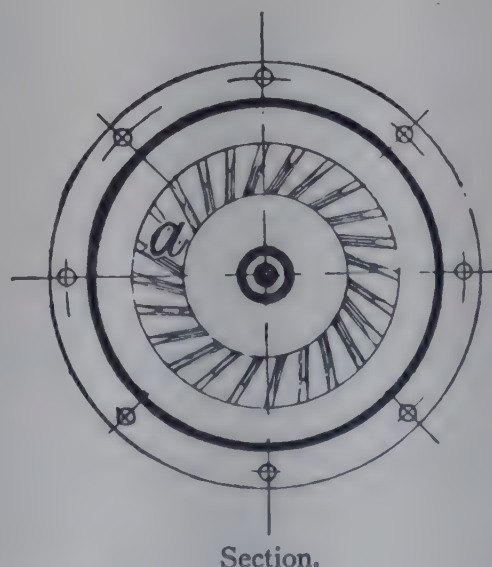
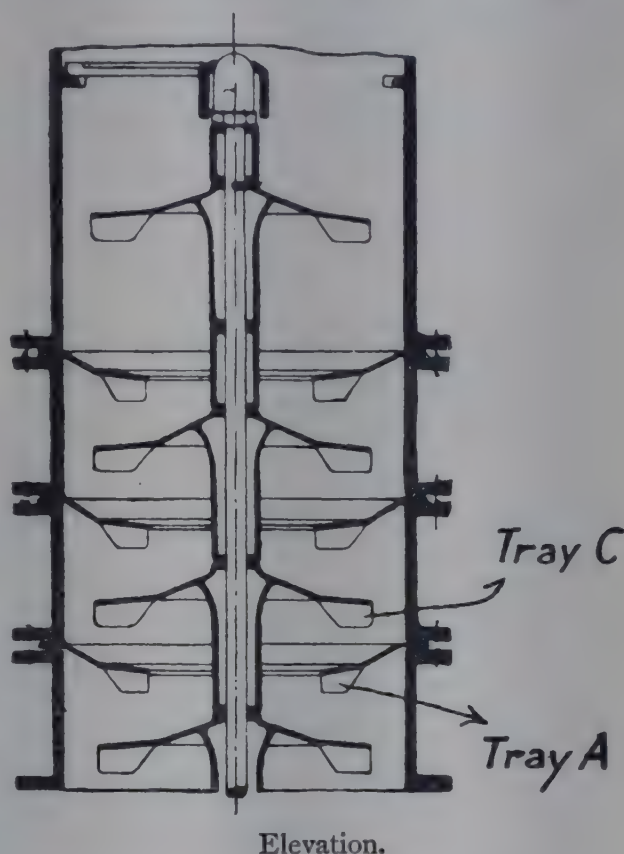


FIG. 134.—Ilges Column.

the condensers *E*, *F* in succession. Pasteurised alcohol is extracted by a pipe *H*, is passed through a refrigerator *G*, and flows away through a test (or sight) glass *P*. Alcohol containing head-products flows away through a pipe *L* to a test-glass *T*. By means of cocks *M* and *N* the quantities of liquid flowing through the test-glasses are regulated to give outflows of pasteurised alcohol and alcohol containing head-products roughly in the proportion of 95 : 5. Suppose, then, that the condenser *E* does not condense its proper proportion of spirit. An excess over that flowing



away through the cock N will then be condensed in the condenser F. By the provision of a pipe R this excess is made to rejoin the spirit running from the condenser E to the top plate of the rectifier. To sum up, let us assume that by means of various other devices we have ensured that the rectifier is working uniformly in other respects so that vapour flows uniformly to the condenser E. We have a constant outflow through cocks M, N. Then by difference we shall have a constant excess of liquid, condensed in E and F, and not passing away through the cocks M, N. This will constitute the reflux or "retrogradation" in the rectifier A, passing steadily down the column from plate to plate to meet the constant upward flow of vapour.

**Continuous Rectifying Apparatus.**—As previously indicated, in rectification the manufacturer has to deal with "phlegms" or alcoholic liquids resulting from the distillation of various types of fermented washes, but all containing head-products (ethers and aldehydes), tail-products (fusel oils), and varying quantities of

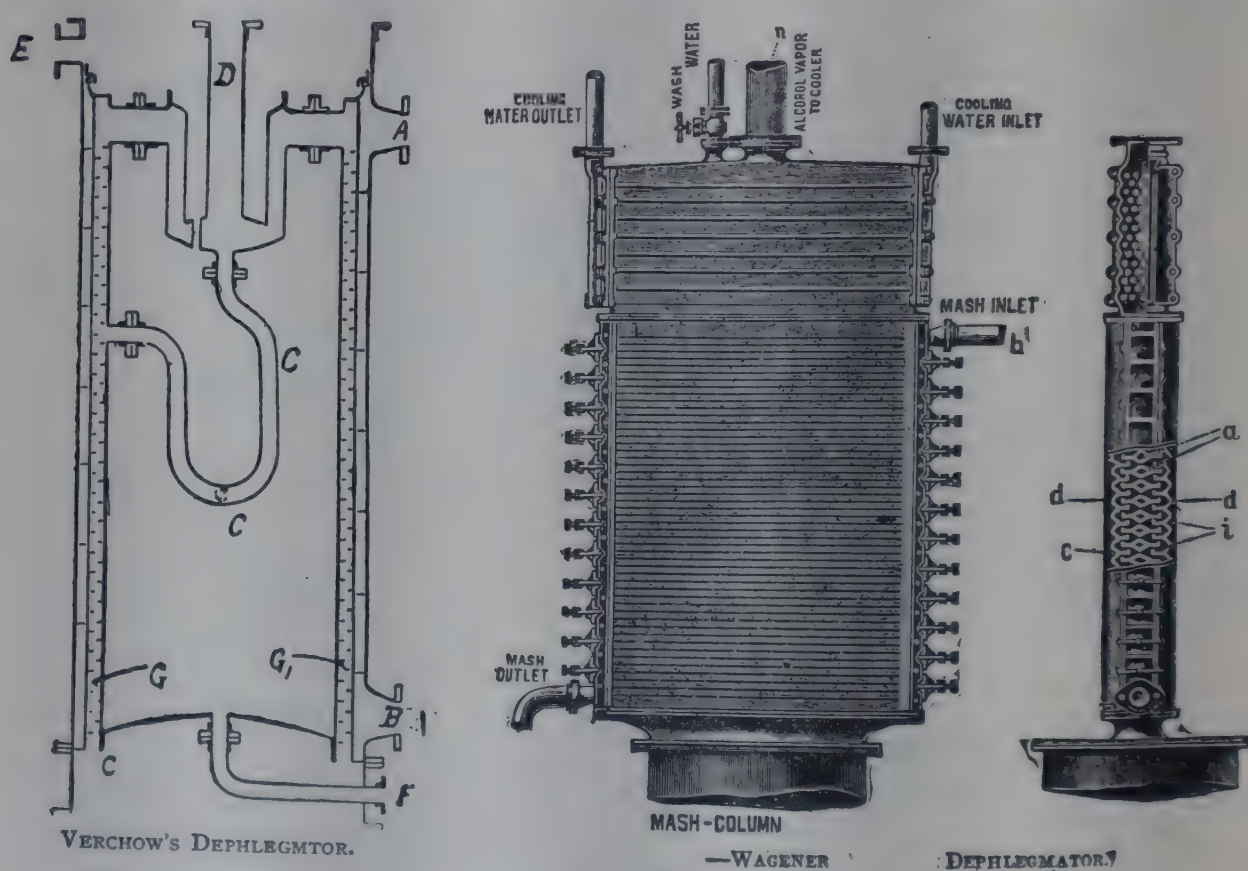


FIG. 135.

water. To get a continuous rectifying apparatus, it is then necessary to effect these operations in apparatus of the columnar type.

Barbet's apparatus is a typical solution of the problem (Fig. 137).

The phlegms (or raw spirit) are first treated for the removal of head-products. This is effected in a **purifying column**, A, to the upper part of which the phlegms are led from the preheater R. The column comprises essentially a distilling column surmounted by a short rectifying column together with the usual condensers B, C. The apparatus is worked in the same manner as an ordinary continuous still, but is so regulated that only about 5 per cent. of distillate is allowed to flow away through the test-glass P. This distillate comprises the most volatile ingredients—the head-products. The alcohol, purified in this manner, flows down to the base of the column A, and thence in the liquid form to the base of a rectifying column G. The rectifying column G also is constructed and worked on the general principles already laid down for continuous distillation. The most volatile ingredient—in this case, the alcohol—passes up the column in the form of vapour, and the less volatile ingredients—water and oils—pass downwards. In order to remove the last traces of head-products, the alcohol is condensed in H, K, and is pasteurised in the manner described on p. 304. The finished alcohol is extracted from the column G, and passes through a refrigerator E to the test glass Q. Alcohol containing traces of head-products issues from the condenser K and passes away through the test-glass R.



The statement that the oils pass downwards with the water is, however, subject to a very important qualification. Duclaux has shown that the tail-products, though themselves less volatile than water, when mixed with water, boil at lower temperatures. Thus a 5 per cent. solution of butyl or amyl alcohol is more easily evaporated than a 5 per cent. solution of ethyl alcohol. In volatilising the whole of the alcohol in the phlegms, one cannot avoid volatilising the whole of the fusel oils. The liquid issuing from the base of the column G is, in consequence, water and nothing but water. The tail-products remain behind in the rectifying column, and if allowed to accumulate would gradually rise from plate to plate until in a continuous plant, such as that described, they would be found in the pasteurised alcohol. It is found that the tail-products accumulate on particular plates, usually the second and third plates below that on which the feed enters. By withdrawing from these plates a quantity of liquid (namely about 2.5 per cent.) such that the amount of oils thus removed is equal to the amount entering within the phlegms, the accumulation of the oils is prevented and the vitiation of the pasteurised alcohol with fusel is prevented. The oil-containing liquid is cooled in a cooler D and passes away through a test-glass T.

The apparatus also comprises steam regulators, and a device for testing the exhaustion of the phlegms, comprising a condenser and a test-glass, which should yield a liquid containing no alcohol. The exhausted phlegms from the base of the rectifier pass to the heat-exchanger R, to heat the incoming phlegms.

Apparatus of this type yield as finished alcohol about 91-92 per cent. of the alcoholic content of the phlegms from which it is derived.

### Combined Distillation and Rectification Stills.—

Recently several firms have placed stills on the market which produce *directly* from the mash at a single operation a perfectly pure spirit at 96-98 per cent. alcoholic strength by volume, entirely free from fusel oil and aldehyde. These stills deliver continuously in four unbroken streams through four different orifices four different products, viz. :—

1. Pure spirit, 96-98 per cent. alcohol, comprising 90 per cent. of the alcohol in the mash, and quite free from fusel oil and acetaldehyde or foreshots.

2. Fusel Oil (tail-products), principally amyl alcohol, which forms an excellent oil for illuminating purposes and for the manufacture of fruit essences.

3. Foreshots, or fore-runnings (head-products), consisting of 97 per cent. acetaldehyde, and containing only 3 per cent. of alcohol. It forms an excellent material for denaturing purposes.

4. The alcohol-free spent wash, used as a food for cattle.

The types used in France and Germany differ to a considerable extent. A plant of each type will be described.

One of the best of the German stills is that of *Robert Ilges*, Germany, manufactured by the firm *Gebrüder Sachsenberg*, of *Rosslau a/Elbe* (Fig. 138).

The apparatus comprises essentially a distilling apparatus, consisting of a still A and a rectifier C, surmounted by a dephlegmator L, which together form a plant yielding alcohol vapours of about 96.5 per cent. free from fusel oil, but containing head-products. These vapours pass by a pipe b to a column D, where the head-products are completely separated.

The still A is of the "full" type devised by Ilges, and described on p. 302. It is fed with wash

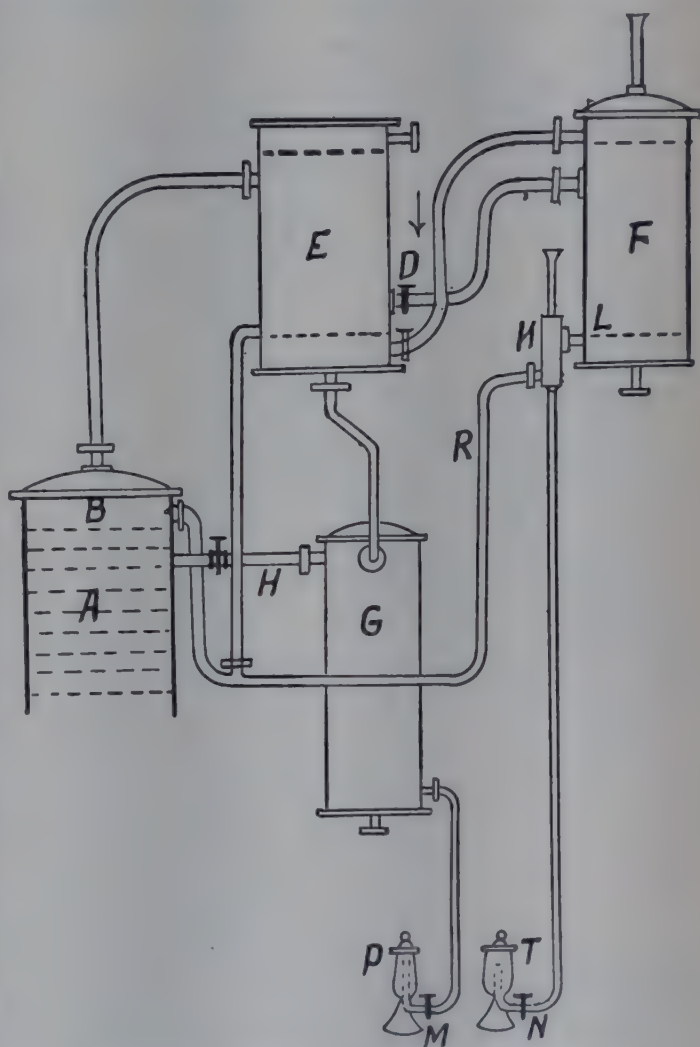


FIG. 136.—Diagram Illustrating Pasteurisation.



in regulated quantity by means of a balance G, on which a funnel 2 is arranged to discharge into the feed pipe 3 of the still. The spent wash is discharged through a regulator B. A regulator F controls the supply of steam to the base *d* of the still.

The vapours evolved in the distilling column A, bearing with them all the easily and difficultly volatile impurities, such as aldehyde and fusel oil, pass through the tube *a* into the first *rectifying column* C, wherein the alcoholic vapours are strengthened to 96½ per cent., and the fusel oil liquefied and separated.

The rectifier C is of the film type devised by Ilges, and is packed with porcelain balls over which the liquid flows in intimate contact with the vapours. The dephlegmator *l* consists of horizontal cooling tubes with a packing of porcelain balls to produce an accompanying rectification.

A plate 8 at the base of the column is so constructed as to allow of the upward passage of vapours only. The liquid collecting on this plate consists of a dilute solution of alcohol containing tail-products, and is led away by a pipe 11 into the cooler J, where it is cooled to 30° C. This

cooling causes the oil to separate completely from the water, and the mixture of oil and water runs into the *oil separator* M. The oil is lighter than the water and floats on its surface. The light oil, therefore, rises in the tube 13, and flows away by a pipe branching out at the point 15, while the water, now freed from oil, but containing alcohol, flows through a pipe 14 into a fusel oil distilling column E, and is distilled free from alcohol by a stream of steam entering at *d*. The alcoholic vapours pass by a pipe 7 to the base of the rectifier C.

After the alcoholic vapours have thus been completely deprived of their fusel oil in the rectifying column C, they enter the second *rectifying column* or purifier D, with a strength of 96.5 per cent. of alcohol by volume, but still containing the volatile **aldehyde and ethers**. It is the function of D to separate the pure alcohol from the aldehyde.

The column D is furnished with dephlegmators *p*, *q*, and tubular heaters *r*, *s*, through which steam circulates, and may conveniently be regarded as divided into three sections. The alcohol vapours of high degree entering the middle section by the pipe *b* are heated by passage through the heater *r* to a temperature sufficient to ensure a satisfactory removal of head-products from the liquid, about 70 per cent. of the vapours entering at *b* retrograding from the dephlegmator *p*. The uncondensed vapours from the dephlegmator *p* (about 30 per cent. of the total) enter the uppermost section and meet liquid (about 20 per cent. of the total) condensed in the dephlegmator *q*. The head-products are thus concentrated in the vapours (constituting 10 per cent. of the vapours entering at *b*) which survive the dephlegmator *q*, and are led by a pipe *c* to a refrigerator L. The liquid from the base of the middle section enters the lowermost section, and is partially vaporised by the heater *s*, to provide an up-flowing current of vapour which removes the last traces of head-products from the down-flowing alcohol. The purified liquid alcohol flows away by a pipe *h* to a refrigerator K.

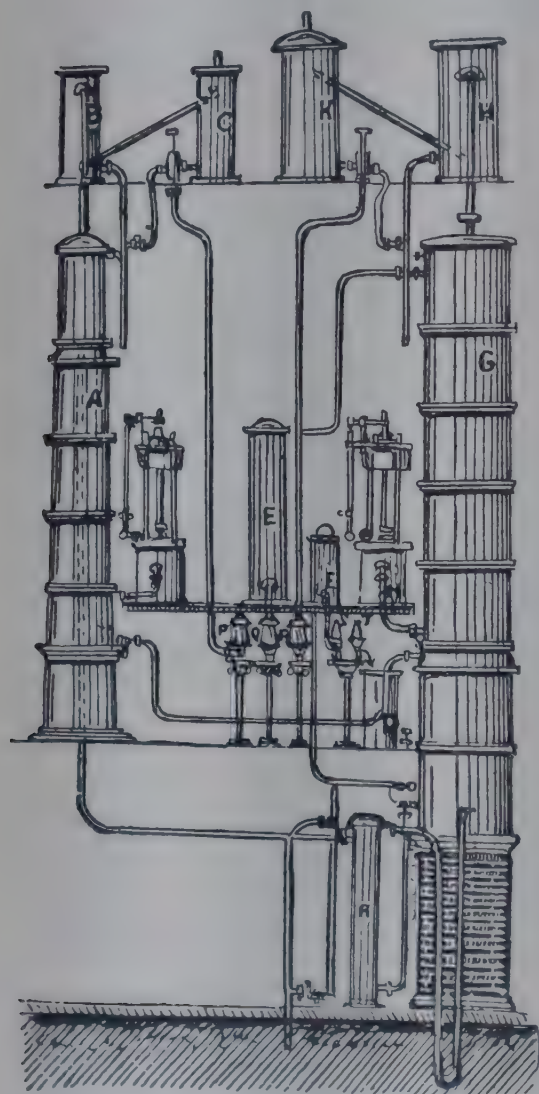


FIG. 137.—Barbet's Continuous Rectifying Plant.

In the German still just described, the alcohol is first concentrated and is then treated for the removal of head-products. In the French still about to be described, it should be noted as a salient feature of difference that the removal of head-products comes immediately after the distillation of the wash, and before the vapours are subjected to rectification. This still was devised by Guillaume and is manufactured by Egrot (Paris). The plant is shown diagrammatically in Fig. 140, and in its actual form in Fig. 139.

The wash is distilled in an inclined column A (Fig. 139) (not shown in Fig. 140) and the vapours enter a heat-exchanger *w* in the base of the rectifying column C, and are there condensed. The resulting phlegms flow through a pipe 3 (Fig. 140) to the purifying column B, where the head-products are volatilised and removed. By an ingenious artifice, to be subsequently described, the tail-products are made to behave as head-products, and are also removed. The purified phlegms pass through a pipe 4 to an accumulator or reservoir V, which is used by the inventor to produce a steadying or



fly-wheel effect on the plant. The phlegms overflow through a pipe 6 to an exhausting column E, which is entirely separate from the column B, and is so shown in Fig. 139, and the vapours there generated are led by a pipe *m* to a concentrating column G. The concentrated alcohol in the liquid form is led by a pipe 12 to the rectifying column C, and is there vaporised by the heat-exchanger *w*. The retrogradation in the column G is a weak spirit containing oils, and is led by a pipe 10 to the purifying-column B.

In the rectifying-column C, the last traces of tail-products are removed in the form of an alcoholic solution, and are led back to the column B by a pipe 25. The liquid alcohol, now almost pure, is led away by a pipe 16 to a final purifying column D, and is there subjected to a partial distillation for the removal of the last traces of head-products. The vapours pass by a pipe 37 to the rectifying column C, and the finished alcohol is led by a pipe 26 to the refrigerator. The condensers at the head of the columns B, C are arranged as described in the article on

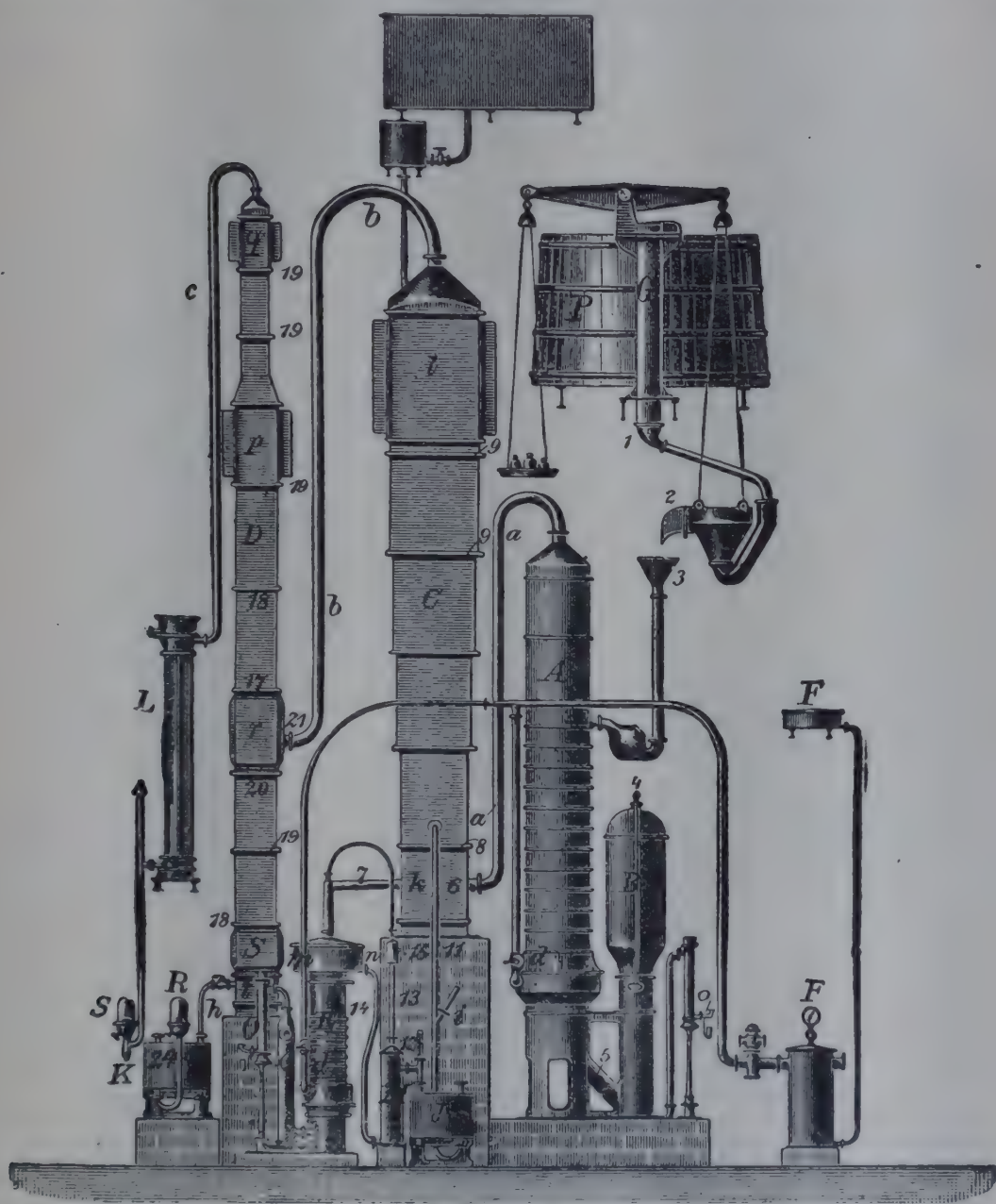


FIG. 138. —Ilges' Combined Distillation and Rectification Apparatus.

**Regulation**, p. 305, and provide distillates of head-products and an alcoholic solution of head-products respectively, the former being led to the refrigerator by a pipe 32, and the latter to the purifying column B by way of a pipe 24.

To return to the removal of the oils in the column B. It was shown in the article on Barbet's rectifying apparatus on p. 306, that fusel oils in the presence of water were more volatile than a dilute solution of alcohol. Guillaume (*vide* British Patent, No. 5,794, 1902), working on this basis, formed the idea of forcing the oils to behave as head-products by keeping the alcohol to the requisite low degree of dilution. In the purifying column, therefore, he provided a pipe 29 admitting water in sufficient quantity to ensure the volatilisation by the uprising vapours of the fusel oils contained in the down-flowing diluted alcohol. Above the point where the pipe 29 enters, the ordinary classification of products takes place, the aldehydes passing upwards as vapour, and the oils retrograding as liquid, and flowing away by a pipe 31 to the refrigerator.



It need scarcely be remarked that this article is far from being exhaustive. An attempt, however, has been made to describe the most important of the principles which have been adopted in the distillation and rectification of alcohol.

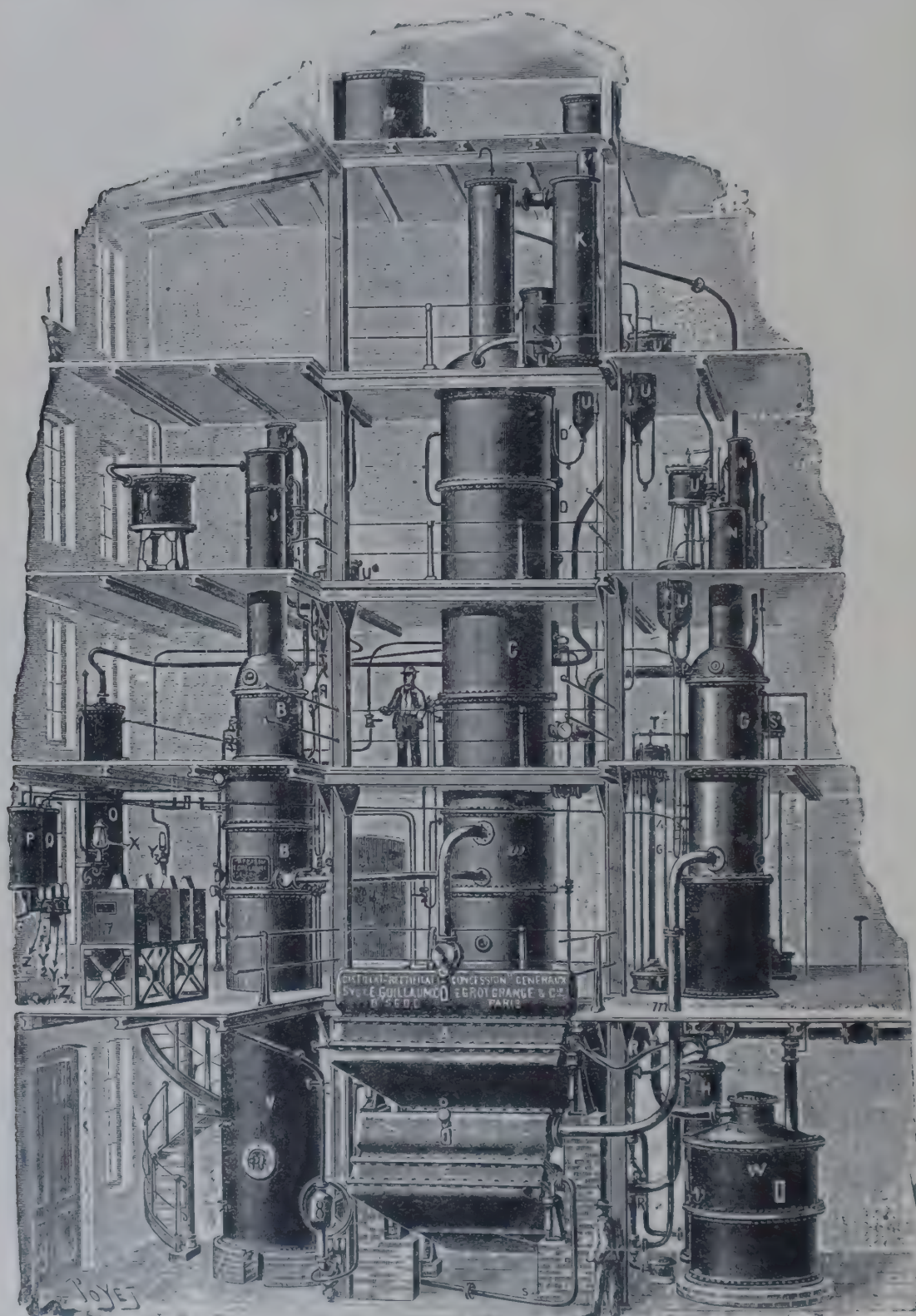


FIG. 139. —Guillaume's Continuous Distillation and Rectification Apparatus.

The plants described accordingly have been those which are most conveniently adapted for a discussion of these principles. It is only fair to say that numerous stills, other than those mentioned—for example, F. Pampe's low-pressure apparatus—are highly efficient and satisfactory in operation.



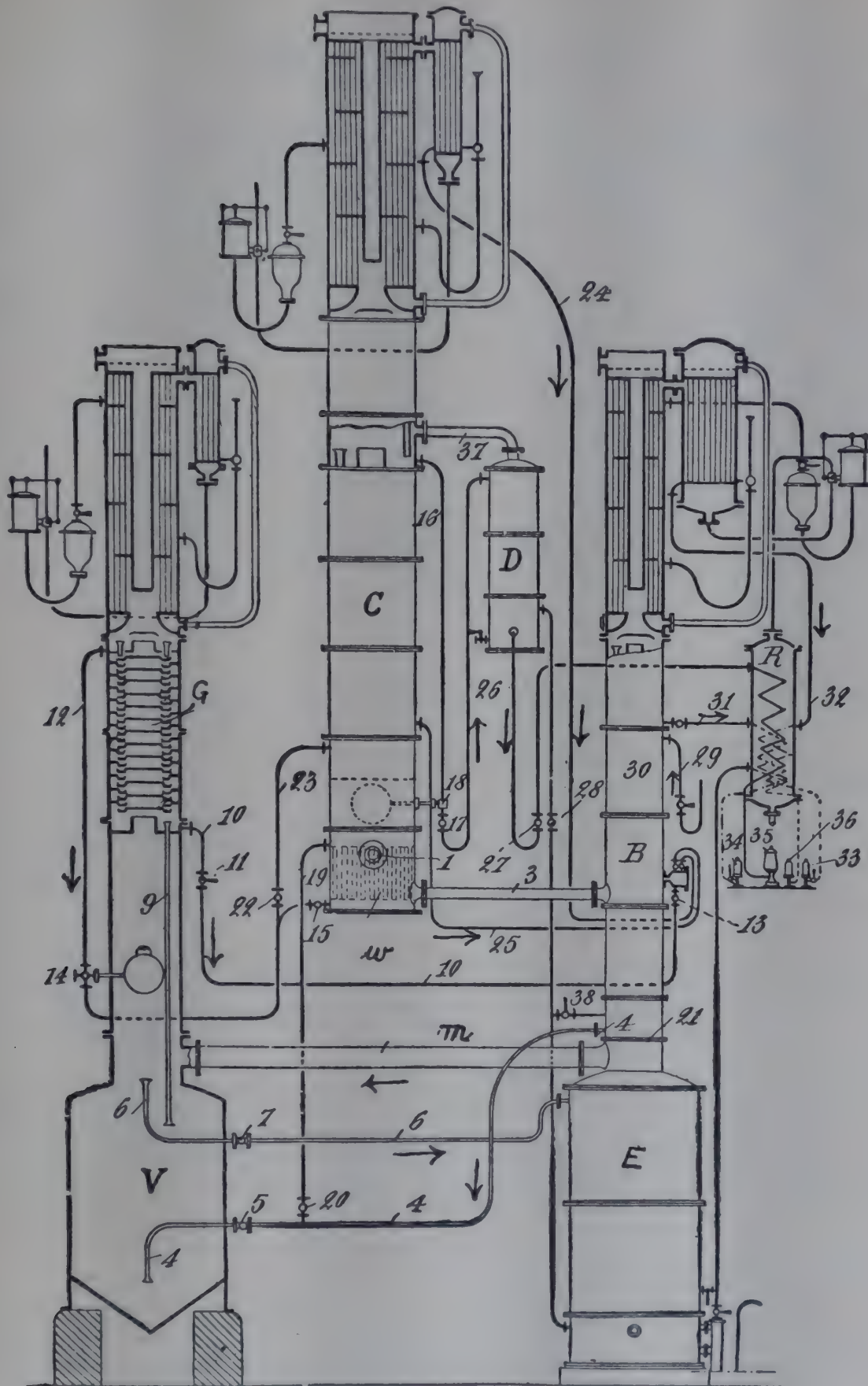


FIG. 140.—Guillaume's Continuous Distillation and Rectification Apparatus: Diagrammatic View.

### STORAGE OF ALCOHOL

The alcohol is stored in large iron tanks, provided with inlet and outlet valves, and similar in construction to petroleum tanks. It is transported, like petroleum, in closed cistern trucks, which are filled and emptied by hose.

### Utilisation of Spent Wash

**The Spent Wash** of corn and potato distilleries resulting after all the alcohol has been distilled off, contains a considerable amount of nitrogen and is used as a food for dairy cattle, beeves, and pigs. The spent wash from potato distilleries is usually made more nutritious by the addition of maize. In Germany the production of these cattle foods has already reached a very high stage of perfection, owing to the numerous "farmer distilleries" which thrive in country districts, such distilleries maintaining their own cattle. These spent washes must be fed warm to the cattle, fresh from the distillation, otherwise they rapidly sour and go bad. Fresh spent wash contains: 1.5-2 per cent. protein, 0.2-1 per cent. fats, 3-5 per cent. carbohydrate, and 90-94 per cent. water.

In large industrial distilleries in towns, where it is impossible to feed the wash to cattle in a fresh condition, the fluid is evaporated and sold as "dry wash." It then contains about 23 per cent. of protein, 35 per cent. of non-nitrogenous extractive substances, 11 per cent. fibres, and 6 per cent. of fat. This **dry wash** is transportable, but not so digestive as the fresh wash.

It has been proposed to place the purified spent yeast on the market as human food (see p. 275).

### Alcoholometry—Testing the Spirit

**Rectified Spirit of Wine**, the most concentrated alcohol producible by ordinary distillation, contains 84 per cent. alcohol, sp. gr. 0.838.

**Proof Spirit** contains 49.24 per cent. alcohol, and has sp. gr. 0.91984 at 60°/60° F. Spirits weaker than this are said by the English Excise to be so many degrees (*i.e.*, so much per cent.) "under proof" (U.P.). Thus a spirit of 20° "under proof" means a liquid containing at 60° F. some 20 volumes of water and 80 volumes of proof spirit. A spirit of 50° U.P. contains 50 volumes water and 50 volumes "proof spirit." Pure water is 100° U.P.

**"Over Proof" (O.P) Spirits** are stronger than "proof spirit," and are defined by the number of volumes of proof spirit 100 volumes could yield when diluted with water. Thus 100 volumes of a spirit "50° O.P." on dilution with water would yield 150 volumes of "proof spirit." Absolute alcohol is 75.25° O.P. and hence 100 volumes when diluted with water can give 175.25 volumes of proof spirit. In the United States "proof spirit" has a sp. gr. 0.9341 at 60°/60° F. and contains 42.7 per cent. by weight of absolute alcohol.

The amount of alcohol in spirit is determined by taking its specific gravity with a hydrometer—here called an "alcoholometer." Pure alcohol at 15.5° C. (60° F.) has a specific gravity of 0.7946. The more water in the liquid, the more nearly the specific gravity approaches unity. The concentration of the alcohol is expressed by volume and by weight. Volume and weight percentages do not correspond, because in mixing water and alcohol a contraction ensues. (50 volumes alcohol + 50 volumes water yield only 96.4 volumes of diluted alcohol.)

**The Volume Percentage**, after Tralles and Brix, gives the number of cubic centimetres absolute alcohol contained in 100 c.c. of the fluid at 15.5° C. (60° F.).

**The Weight Percentage** (adopted officially since 1888 in Germany) gives the number of grams of absolute alcohol contained in 100 g. of the spirit at 15° C.

The "apparent" alcohol percentage, as read off on the graduations on the hydrometer immersed in the spirit at any given temperature, is reduced to the "True" alcohol percentage at the standard temperature, 15° C. in Germany, and 60° F. in England, by means of special tables.

The spirit is sold on the basis of the amount of absolute alcohol (100 per cent.) it contains. The percentage of alcohol by volume and weight contained in watery solutions of various specific gravities is expressed by the following table:—



**SPECIFIC GRAVITY OF PERCENTAGE MIXTURES OF ALCOHOL AND WATER BY  
VOLUME AND BY WEIGHT AT 60° F. (15<sup>5</sup>/<sub>9</sub>° C.)**

Per Cent. Alcohol.	Per Cent. by Volume.	Per Cent. by Weight.	Per Cent. Alcohol.	Per Cent. by Volume.	Per Cent. by Weight.	Per Cent. Alcohol.	Per Cent. by Volume.	Per Cent. by Weight.
	Corresponding Specific Gravity.			Corresponding Specific Gravity.			Corresponding Specific Gravity.	
1	0.9985	0.9981	35	0.9592	0.9490	69	0.8925	0.8748
2	.9970	.9963	36	.9579	.9472	70	.8900	.8724
3	.9956	.9944	37	.9565	.9453	71	.8875	.8700
4	.9942	.9928	38	.9550	.9433	72	.8850	.8676
5	.9928	.9912	39	.9535	.9413	73	.8825	.8652
6	.9915	.9896	40	.9519	.9394	74	.8799	.8629
7	.9902	.9880	41	.9503	.9374	75	.8773	.8605
8	.9890	.9866	42	.9487	.9353	76	.8747	.8581
9	.9878	.9852	43	.9470	.9332	77	.8720	.8557
10	.9866	.9839	44	.9452	.9311	78	.8693	.8533
11	.9854	.9826	45	.9435	.9291	79	.8666	.8509
12	.9843	.9813	46	.9417	.9269	80	.8639	.8484
13	.9832	.9800	47	.9399	.9248	81	.8611	.8459
14	.9821	.9788	48	.9381	.9227	82	.8583	.8435
15	.9811	.9775	49	.9362	.9204	83	.8555	.8409
16	.9800	.9763	50	.9343	.9183	84	.8526	.8385
17	.9790	.9751	51	.9323	.9160	85	.8496	.8359
18	.9780	.9739	52	.9303	.9138	86	.8466	.8333
19	.9770	.9727	53	.9283	.9116	87	.8436	.8307
20	.9760	.9714	54	.9263	.9094	88	.8405	.8282
21	.9750	.9702	55	.9242	.9072	89	.8373	.8256
22	.9740	.9690	56	.9221	.9049	90	.8339	.8229
23	.9729	.9677	57	.9200	.9027	91	.8306	.8203
24	.9719	.9664	58	.9178	.9004	92	.8272	.8176
25	.9709	.9651	59	.9156	.8981	93	.8237	.8149
26	.9698	.9637	60	.9134	.8958	94	.8201	.8122
27	.9688	.9622	61	.9112	.8935	95	.8164	.8094
28	.9677	.9607	62	.9090	.8911	96	.8125	.8065
29	.9666	.9592	63	.9067	.8888	97	.8084	.8036
30	.9655	.9577	64	.9044	.8865	98	.8041	.8006
31	.9643	.9560	65	.9021	.8842	99	.7995	.7976
32	.9631	.9544	66	.8997	.8818	100	.7946	.7946
33	.9618	.9526	67	.8973	.8795			
34	.9605	.9508	68	.8949	.8772			

The spirit is also usually subjected to the following tests (for fuller details, see Allen's "Commercial Analysis," 1909, vol. i.):—

1. **Amount of Fusel Oil** (Higher alcohols).—In England and America this is usually estimated by the *Allen-Marquart* method, which consists in boiling the sample with KOH, steam distilling, adding saturated brine to distillate to separate fusel oil, and extracting with  $\text{CCl}_4$ , oxidising with  $\text{K}_2\text{Cr}_2\text{O}_7 + \text{H}_2\text{SO}_4$ , titrating with  $\frac{\text{N}}{10} \text{Ba}(\text{OH})_2$ , using methyl orange as indicator at first, and then

phenolphthalein. Each c.c. of  $\frac{\text{N}}{10}$  alkali required in the second stage of the titration (using phenolphthalein) corresponds to 0.0088 g. amyl alcohol. The official German method (Röse-Herzfeld) is to shake the spirit with chloroform under rigorously defined conditions. The increase of volume gives the amount of fusel oil.

2. **Aldehyde Determination**.—This is estimated colorimetrically by means of Schiff's reagent.

3. The **Furfurol** is estimated by comparing the tint produced in the liquid by the addition of aniline acetate with that produced in a standard solution of furfurol in pure 50 per cent. alcohol. A first-class prima spirit should contain 94 per cent. alcohol by weight (96 by volume), possess a neutral taste and smell, be of a white colour, be quite neutral, contain no aldehyde or furfurol; should remain clear and colourless when mixed with water; with  $\text{KMnO}_4$  solution should remain red after thirty minutes; boiled with  $\text{H}_2\text{SO}_4$  (Savalle's test) should give no colour; treated with  $\text{H}_2\text{SO}_4$  in the cold (Vitali's test) should give no colour.

**Acknowledgment**.—The authors have much pleasure in thanking the firm of John Dewar & Sons Ltd., distillers, of Perth, for much help and scientific information regarding alcohol manufacture, which, in their hands, has already reached a very high state of perfection.



## Fusel Oils and the Manufacture of Amyl and Butyl Alcohol

Whisky, brandies, and similar alcoholic fluids sometimes contain as much as 0.6 per cent. of fusel oils, which contain esters, and are of value in giving a characteristic odour to the liquid. Potato spirit fusel oils have an unpleasant taste and smell.

It is the *quality*, not so much as the *quantity*, of the fusel oil present in a spirit which affects its taste, and decides whether it must be refined or not. Many valuers rely on taste alone for the determination of this important point.

Fusel oil was until recently an almost valueless by-product of the spirit industry, but is now a very valuable substance.

**Manufacture.**—The manufacture by the distillation of wine and especially spirits has been described above (pp. 251, 298, 300, 307, 308, 309). By the processes above described it was necessary to manufacture 1,000 parts of ethyl alcohol for every one of fusel oil produced. *Prof. Fernbach* of the Pasteur Institute has worked out a process whereby starch is directly fermented to fusel oil and acetone. Mashers are made of cereal grains (*e.g.*, maize) or potatoes, and inoculated with special cultures, whereby over 42 per cent. of the starch employed is converted into mixed higher alcohols (fusel oils) and, *Fernbach* states, of these about 65 per cent. is butyl alcohol. *O. Hehner* found that 100 parts of the dried substance of potatoes yielded 43 parts of higher alcohols plus acetone, the latter constituting above one-third. It is asserted that these fusel oils can be placed on the market at a price not exceeding £35-£45 per ton (see *W. H. Perkin, jun., Journ. Soc. Chem. Ind., 1912, p. 622*; also English Patents, 15,203, 1911; 15,204, 1911; 21,073 1912).

**Composition of Fusel Oils.**—The composition of **Wine Fusel Oils** is given on p. 251. They consist, roughly, of 51 per cent. *normal butyl alcohol*, 20 per cent. *amyl alcohol*, 10 per cent. *normal propyl alcohol*, 8 per cent. *ethyl acetate*, 8 per cent. *acetal*, and small amounts of *esters of fatty acids, acetaldehyde, heptyl alcohol, amine bases*, etc.

The composition of **Spirit Fusel Oils** varies considerably with the method of manufacture, but consists mainly of *amyl alcohol*. *W. E. Bell* gives the following analysis of a sample of the fusel oils removed from the "hot feints" receiver of a Coffey Still (p. 298):—

*Amyl alcohol* (B.P. 132° C.), 42.2 per cent.; *isobutyl alcohol* (B.P. 109° C.), 33.4 per cent.; *normal propyl alcohol* (B.P. 97° C.), 18.9 per cent.; *ethyl alcohol*, 5.5 per cent. Ethyl esters of palmitic and oleic acid were also present.

A sample of **Commercial Fusel Oil** contained: *Amyl alcohol* (B.P. 132° C.), 68 per cent.; *isobutyl alcohol* (B.P. 109° C.), 24 per cent.; *normal propyl alcohol* (B.P. 97°), 7 per cent.; small quantities of *esters, furfural*, etc.

When commercial fusel oil is fractionated the portions boiling at 128°-131° C. consist of the **Amyl Alcohols**, containing 87 per cent. **isoamyl alcohol**,  $(\text{CH}_3)_2\text{CH}.\text{CH}_2.\text{CH}_2\text{OH}$ , and 13 per cent. **active amyl alcohol**,  $\text{CH}_3.\text{CH}_2\text{CH}(\text{CH}_3).\text{CH}_2\text{OH}$ .

The fusel oil produced by **Fernbach's Fermentation Process** contains about 65 per cent. of **butyl alcohol**.

**Uses of Fusel Oils and Higher Alcohols.**—Fusel oil was, until recently, used as an illuminating oil, but is now far too expensive for this purpose. It is very largely used for manufacturing the individual higher alcohols (by fractional distillation) and their esters, thus giving rise to the industry of **Fruit Essences** (see p. 382) for flavouring liquors, jellies, sweets, etc. Very large quantities of **amyl acetate** are used as a solvent for pyroxyline (nitrocellulose) for the purpose of making nitrocellulose varnishes, lacquers, and for artificial leathers having a nitrocellulose composition (see pp. 49, 383, 589). It was formerly employed as a solvent in the explosive and paint industry, but its high price has caused an abandonment of it in favour of cheaper solvents. **Amyl alcohol** is used in the flotation process of separating sulphide ores, its usefulness depending upon the low surface tension of its aqueous solution. Fusel oil and its constituent alcohols have been employed for the precipitation of asphalt from heavy mineral oils. Recently the *Synthetic Products Company* of London have proposed to place it on the market by *Fernbach's Fermentation Process*, and to utilise the product for the manufacture of **synthetic rubber** by methods worked out by *Perkins, Matthews, and others* (see *W. H. Perkins, Journ. Soc. Chem. Ind., 1912, pp. 620-623*). **Butyl alcohol** is stated to be an excellent "Burn" cure.

**Statistics.**—In Germany in 1900-1901 the oil sold at 50 M. for 100 kilos, or 4½ lbs. a shilling. By 1910 its price had risen to 170 M. per 100 kilos. In 1912 it was quoted at £140 a ton. The world's supply in 1912 was variously estimated at 3,500 to 6,000 tons annually, and until recently it was necessary to manufacture 1,000 parts of alcohol for every one of fusel oil. By *Fernbach's Fermentation Process* it is stated that it can be produced in unlimited amount at £35-£40 a ton. The *United States* in 1910 imported 4,954,000 lbs. (value, \$598,000) of fusel oil, Russia supplying one-third of the quantity. No less than 450,000 gals. of **amyl acetate** are annually consumed in the *United States* for solvent purposes (nitrocellulose varnishes).

For modern statistics see Appendix III.



## VI.—VINEGAR, LACTIC ACID, BUTYRIC ACID

BY G. MARTIN, Ph.D., D.Sc.

## VINEGAR

## LITERATURE

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ROTHENBACH.—“Organismen des Gärungsessigs.” 1907.

For **Acetic Acid** see under **Destructive Distillation of Wood**. For **Acetic Acid Bacteria** see under **Bacteria**, p. 224.

Vinegar consists of a weak solution (4-10 per cent.) of acetic acid in aqueous liquors prepared by the oxidation of alcoholic liquors by means of acetic acid bacteria, *Bacterium aceti*, many varieties of which exist, the best races being propagated by pure culture methods (see p. 231) and used for impregnating the alcoholic liquors to be fermented.

The *Bacterium aceti* will not grow in a pure aqueous solution of alcohol; they require, besides alcohol, the presence of nitrogenous matter and salts to serve as food. Consequently the starting-point in the manufacture of vinegar consists of an alcoholic liquor such as wine, beer, and alcoholic mashes generally.

The bulk of English made vinegar is manufactured from **malt**, or a mixture of malt with grain and sugar. The malt or malt and grain is crushed, and heated in a mash-tun with water at a gradually increasing temperature until the starch is converted into sugar by the diastase in the malt, as described under **Brewing**, the resulting liquid being known as **wort**.

Often the wort is obtained by the **conversion process**. The grain, usually rice or maize and free from malt, is treated with dilute  $H_2SO_4$  in a closed vessel termed a **converter**. The acid hydrolyses the starch to produce a saccharine solution which is then freed from acid by calcium carbonate, and the liquor separated from the precipitated calcium sulphate.

The wort is now pitched with yeast and is aerated and kept at the right temperature so as to convert as much as possible of the sugar into alcohol. The subsequent strength of the vinegar depends largely upon the success of this stage, because all saccharine matter (also dextrines) escaping the action of the yeast also

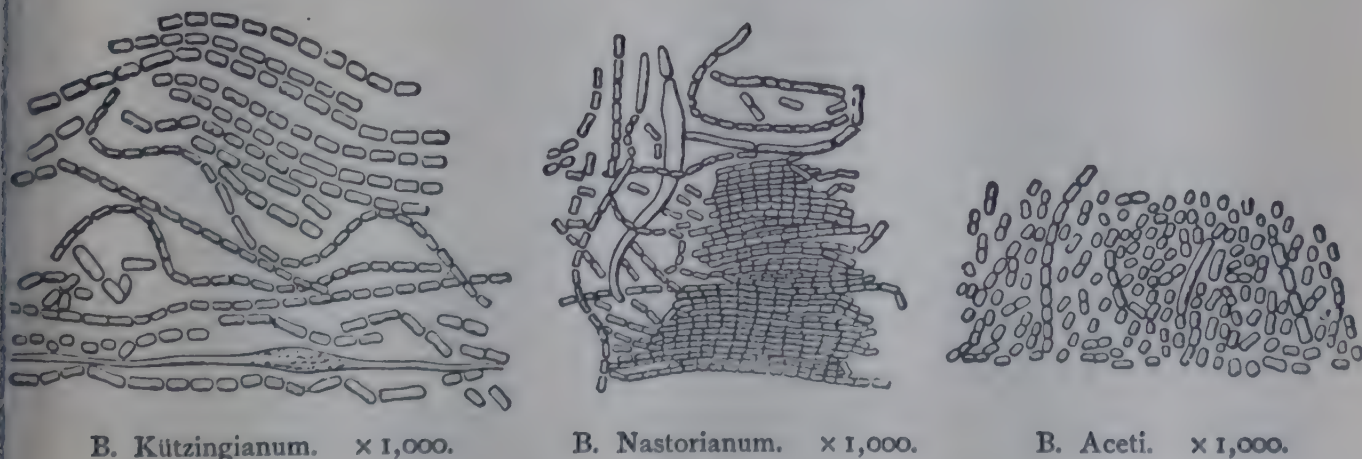
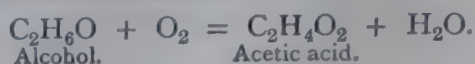


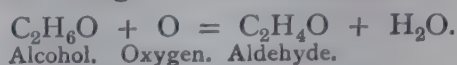
FIG. 141.—Acetic Acid Bacteria (Hansen).



remain unattacked by the acetic bacteria. The resulting liquor, called **gyle**, and containing 6-7 per cent. of alcohol, is treated with the acetic acid bacteria, the alcohol being oxidised to acetic acid, thus:—



Many other compounds are simultaneously formed, especially aldehyde, which is produced as an intermediate stage in the oxidation:—



The acetifiers employed consist of a large wooden vat provided with a perforated false bottom and numerous holes in the sides for the admission of air. The interior of the vat is filled with basket-work (formerly beech shavings), and a rotating sparger is used for sprinkling the gyle uniformly over the material.

Fig. 142 shows a section of the upper portion of an acetifier. The gyle, impregnated with acetic acid bacteria, is pumped from the bottom of the vat and discharged into the funnel at the top, which is boxed in to prevent loss by evaporation. The liquid flows down the tube G, enters the sparger R, which revolves on the pivot S. In the arms of the sparger are a number of small holes through which the liquid rushes, thus causing the sparger to revolve steadily and uniformly sprinkle the surface of the basket-work. The acetic bacteria multiply on the surfaces of the basket-work, generating heat and rapidly oxidising the alcohol as it passes over them. A thermometer inserted through a hole in the side of the acetifier indicates the temperature within.

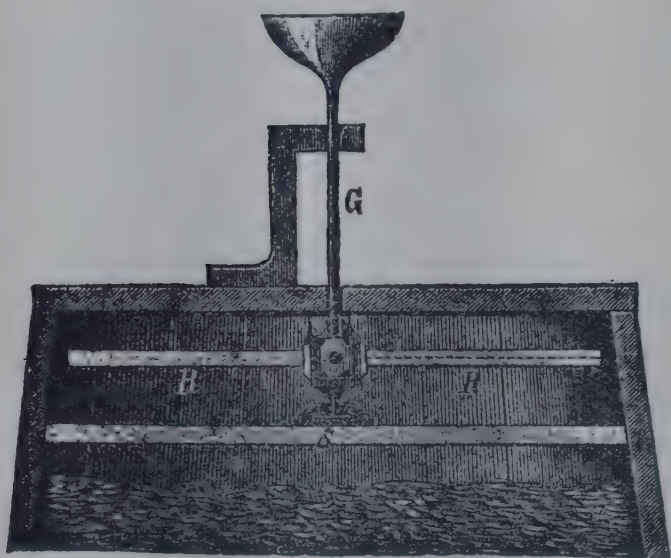


FIG. 142.—Section of the Upper Part of Modern Acetifier.

(After C. A. Mitchell. See *Knowledge*, June 1911.)

According to Mitchell (see above) the species of acetic bacteria most used in England are most active at 105° F. (40.6° C.) and flourish well at 110° F. (43.3° C.). The bacteria used on the Continent are seldom worked above 95° F.

For successful working the conditions are: (1) a regular and uniform supply of air to the bacteria; (2) maintenance of the correct temperature in the acetifier. In the presence of too much air the bacteria oxidise part of the acetic acid to CO<sub>2</sub>, and the resulting vinegar is weak. On the other hand if too little air is supplied the bacteria unite together into a slimy mass (mother-of-vinegar) by the swelling and fusion together of their outside cellular membranes, thus converting themselves into a "zoogloal form" and clogging up the acetifier with slimy masses which still further impede the entrance of air and stop uniform aeration.

The finished vinegar flowing out at the bottom of the apparatus usually contains a very small percentage of alcohol, because unless some alcohol is present the bacteria attack the acetic acid, oxidising it further, thus occasioning a loss. The vinegar leaving the acetifiers is stored for some time in order to form the pleasant smelling esters to which vinegar owes its aroma. It is then clarified by filtration through fine sand or similar substance. As it leaves the filters the vinegar contains 6 per cent. acetic acid and upwards. It is diluted to the proper strength and sent out to the trade.

A "24" vinegar contains 5.5 per cent. of acetic acid, and upwards. Weaker vinegars are known as "22," "20," "18," and "16," the latter of these containing 4.1 per cent. of acid. The numbers originally referred to the number of grains of sodium carbonate required to neutralise the acid in one fluid ounce of the vinegar.



A very cheap vinegar containing 3.5 per cent. of vinegar is sometimes sold under the name "Diamond." Usually, however, vinegars contain more than 4 per cent. of acetic acid. The yield of acetic acid is usually about 70-80 per cent. of theory, the loss of acidity due to evaporation of the alcohol and destruction of acetic acid (due to irregular aeration) ranging from 10-20 per cent., and sometimes, in faulty apparatus, even to 30 per cent.

Cheap vinegars are sometimes "faked" by diluting distilled acetic acid (obtained from wood) with water to the proper degree, and colouring it with caramel or burnt sugar. Some vinegars are aromatised with fennel, caraway, and similar substances, others are coloured red, and some are even adulterated with dilute  $\text{H}_2\text{SO}_4$ .

**Wine Vinegar** is not manufactured in England on account of the absence of wine. On the Continent, however, it is an important industry. The wine (usually a sour kind of poor quality) is treated with acetic acid bacteria, and in the quick process is allowed to flow through vats containing beech shavings or basket-work as above described. The best **wine vinegars**, however, are made by the **Orleans Process**. Oaken vats, of 2-4 hl. capacity, and provided with air-holes in their upper parts, are placed in chambers kept at  $20^\circ$ - $25^\circ$  C., and one-fifth filled with a hot strong wine vinegar; this partially soaks into the wood and deprives it of its woody taste. Next 10 l. of wine are added, and the liquid allowed to stand, usually after impregnating it with a small amount of a pure culture of acetic acid bacteria. The bacteria develop rapidly, covering the liquid with a film of slimy "mother-of-vinegar." The alcohol is oxidised to acetic acid, which sinks to the lower part of the liquid, the light alcohol accumulating gradually at the surface. After about a week another 10 l. of wine are added, and the process repeated until the vat is half full. Then a third of the finished vinegar is withdrawn, and the addition of wine continued as before. Wine vinegar is much valued for its pleasant bouquet.

Vinegar is used for flavouring meat, etc., and also for making white lead (which see).

**Statistics.**—The English imports of **Vinegar** and **Acetic Acid** for table use: 1906, 258,089 gals.; 1908, 459,502 gals.; 1910, 212,696 gals.; value in 1910=£13,400. The export was: 1906, 569,182 gals.; 1908, 768,742 gals.; 1910, 880,017 gals.; value in 1910=£105,800. The U.S.A. in 1910 imported 310,000 gals. (value \$79,000), and exported 115,000 gals. (value \$13,000).

For modern statistics see Appendix III.

## LACTIC ACID, $\text{CH}_3\text{CH}(\text{OH})\text{COOH}$

### LITERATURE

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Ethylidene lactic acid is now prepared on a large scale in America, Great Britain, and Europe. It is a rapidly growing industry—a result due to the recent introduction of pure cultures of the lactic acid bacillus into the industry. In England the industry has been in existence for nearly thirty years, being originated by Mr Avery by processes patented between 1881-1884.



In Germany up to 1895 no factory existed for the supply of lactic acid, all the lactic acid being imported from England. At the present time thirty factories have since come into existence, the largest being the Firm C. H. Böhringer u. Sohn in N. Ingelheim. This latter firm alone produces 500,000 kg. of technical lactic acid. In the *United States* the industry is an old and well-established one; thus so long ago as 1895 the *United States* consumed 1,000,000 lbs. and exported 500,000 lbs. In 1896 the domestic consumption was 1,200,000, and the foreign 1,000,000 lbs.

The manufacture is carried out by allowing the micro-organism known as *Bacillus acidi lactici* (of which there exist many races) to split up by fermentation a solution containing grape sugar, when the following change takes place:—



### Avery's Process

**Preparation of the Saccharine Solution.**—The solution should have a sp. gr. of 1.05-1.075, and contain  $7\frac{1}{2}$ -11 per cent. of glucose. It is advantageous to replace 10-15 per cent. of the glucose by cane sugar, which is progressively inverted by the lactic acid, and this continually furnishes fresh matter for the bacillus. The solution should contain nitrogenous food (not under 2 parts nitrogen to 100 parts sugar in vat) for the bacillus. An extract of vegetable albumen, made by extracting bran with boiling water and dilute acid, is very suitable; or mineral nitrates and ammonium salts may be used.

**Process of Impregnation.**—The saccharine solution made up as described above is boiled for one hour to sterilise it, rapidly cooled between 55° C. and 45° C., run into the fermentation vat, and impregnated with the *Bacillus acidi lactici*. In continuous manufacture the impregnation is carried out by running in 20 per cent. or more of a preceding fermenting liquor, in which a lively fermentation is in progress. But for the original impregnation a good culture of the lactic bacteria must be obtained by allowing milk to stand at 45° C. until slightly sour. A pure culture is usually obtained by impregnating previously sterilised milk, kept at 45° C., with a good lactic acid bacteria obtained from the bacteria in a ferment tank. The best variety of *Bacillus acidi lactici* is 2-2.5  $\mu$  long, and 1  $\mu$  in diameter.

**Process of Fermentation.**—During the process of fermentation the temperature of the saccharine liquid is kept between 45° and 55° C. in order to avoid the development in the liquid of butyric acid or alcoholic ferments. Since the *Bacillus acidi lactici* cannot flourish in solutions containing more than 1 per cent. of lactic acid, the acid as it is produced is continually removed by the addition of chalk dust suspended in water, in such proportion as to keep the lactic acid within the limits 0.02-0.5 per cent. If the neutralisation is carried too far, so as to lower the percentage of lactic acid below these limits, butyric acid fermentation may set in and spoil the yield. The fermentation should proceed vigorously and be completed in three to six days when 98 per cent. of sugar is used up. The liquor, which is a solution of calcium lactate, is then heated sharply to kill all bacteria and spores, filtered from the dead bodies of the bacteria, and evaporated. Pure lactic acid may be obtained by repeated crystallisation of the calcium lactate; but a commercial lactic acid is obtained merely by decomposition of the uncrystallised solution by sulphuric acid. The free acid is filtered from the  $\text{CaSO}_4$  (which is practically insoluble in the dilute lactic acid) and evaporated to a 50 per cent. solution, when it forms a brownish syrupy liquid, of sp. gr. 1.20, containing about 7 per cent. lactic anhydride.



**German Methods of Manufacture.**—The solution of grape sugar is always made from a mash of starchy material (maize, potatoes, rice, etc.) by treating with malt in order to convert the starch into maltose, just as in the manufacture of spirits. The lactic acid bacillus employed in the largest German factories is the *Bacillus acidi lactici*, Hüppe, forming short thin rods ( $6\ \mu$ . and more long), linked together in chains; it is sporeless. A pure culture of this bacillus is obtained by the ordinary methods of bacteriology from sour milk or cheese, using as growing medium a solution of 100 parts grape sugar, 1 part dried peptone, 0.2 part potassium hydrogen phosphate, 1 part sal-ammoniac, 50 parts of powdered chalk, and 600 parts of water.

The fermentation is carried out, much as in Avery's process, at a temperature of  $45^{\circ}$ ; but the time of fermentation is usually ten to twelve days. At the end of this time the absence of sugar is proved by Fehling's solution, the mass is then made weakly alkaline with lime water, boiled, filtered, and evaporated to  $15^{\circ}$  Bé., when the calcium lactate crystallises out and is filter-pressed away from the dark mother-liquors, which, united with the washings, are again evaporated to  $15^{\circ}$  Bé. and allowed to crystallise, the black mother-liquors running to waste.

The calcium lactate is purified by crystallising and decomposed by  $\text{H}_2\text{SO}_4$ , filter-pressed from the precipitated  $\text{CaSO}_4$ , and the solution of the acid concentrated by evaporation. If a clear lactic acid solution is required, the warm solution of lactic acid from the gypsum filter presses is pumped into tall wooden or leaden cylinders filled with animal charcoal, left there for some hours, drawn off at the bottom, filtered through felt cloth, and evaporated to 50 per cent. acid.

Chemically pure lactic acid is obtained by decomposing calcium lactate with zinc carbonate, whereby the sparingly soluble and easily crystallisable zinc lactate is obtained. The pure zinc lactate is then decomposed by  $\text{H}_2\text{S}$ , filtered from the  $\text{ZnS}$ —a difficult operation rendered easier by adding animal charcoal, paper pulp, etc.—and evaporated in an enamelled vacuum apparatus; when clear, pure lactic acid is obtained.)

It is also obtained pure by distilling syrupy ( $26^{\circ}$  Bé.) commercial lactic acid with superheated steam at  $140^{\circ}$ – $160^{\circ}$  C. from a calcium chloride bath. At  $140^{\circ}$  C. acetic acid, butyric acid, etc., distils, then comes pure lactic acid or anhydride. The concentrated distillate is decolourised by sunlight, animal charcoal, etc. 20–30 per cent. of the lactic acid is lost owing to the formation of lactic anhydride.

Another method is to shake the lactic acid for twenty-four hours with three times its volume of ether in a glass balloon. The impurities settle on the walls of the vessel. The clear ethereal solution is then forced by means of compressed air into another glass balloon, is there decolourised with animal charcoal, filtered through paper or cotton cloth, the ether distilled over and used again, and traces of the ether in the acid removed by blowing in warm air.

A proposed method (German Patent, 171,835) of purification is to convert the lactic acid into its ethyl ester (by boiling with ethyl alcohol and a little normal acid) and distilling *in vacuo*. The pure ester thus obtained is then decomposed by blowing through steam, the alcohol distilling over and the lactic acid remaining, being concentrated by evaporation.

The pure acid costs five to six times as much as the commercial variety.

**Properties.**—Pure anhydrous lactic acid, obtained by repeated rectification *in vacuo*, is a crystalline mass—M.P.  $18^{\circ}$  C.; B.P.  $119^{\circ}$ – $120^{\circ}$ .

Commercial pure 75 per cent. lactic acid is a syrupy, clear fluid, containing 8 per cent. lactic anhydride.

**Salts.**—The calcium and zinc salts occur in commerce, forming a convenient means for transport of lactic acid. The iron salt is used medicinally. Antimony lactate is used to an increasing extent as a substitute for tartar emetic in dyeing and printing calico. Certain double salts of antimony lactate with alkalis, alkaline earths, and zinc salts are largely manufactured for the purpose under such names as *Lactolin*, *Antimonin*. For preparation see German Patents, 98,939, 136,135, 148,069.

The **Titanium salts** (German Patents, 136,009, 149,577) are used in dyeing leather.

**Uses.**—See above, under **Salts**. Lactic acid, since its increased production and consequent fall in price, is used to a very large extent in dyeing wool as an assistant in mordanting with potassium bichromate. It is also largely used in tanning for removing the lime from the skin (J. T. Wood, *Journ. Chem. Ind.*, 1885, 27 *et seq.*; F. Andreasch, *Der Gerber*, 21, 506; 22, 513). It is used to a limited extent in spirit manufacture for souring the yeast in order to prevent the development of injurious fermentation.

**Statistics.**—*German Imports*: 1909, 30 dz.\*; 1908, 20 dz. *Exports*: 1909, 10,470 dz.; 1908, 9,720 dz.

The English exports are very considerable, but owing to the haphazard way the materials exported are classified no information is obtainable from the Custom House returns.

For modern statistics see Appendix III.

## BUTYRIC ACID

Normal butyric acid,  $\text{CH}_3(\text{CH}_2)_2\text{COOH}$ , is usually obtained in a similar manner to lactic acid (above described) by fermentation of sugar or starch in the presence of calcium carbonate. Formerly the fermentation was effected by adding to the solution small amounts of decaying cheese, and keeping the solution at  $25^\circ\text{--}35^\circ\text{C}$ . Now, however, the liquor is usually impregnated with pure cultures of butyric acid bacteria. According to Fitz (*"Ber."* II, 49, 53) cultures of *Bacillus subtilis* and *Bacillus bovocapricus* are especially efficient. The calcium butyrate resulting from the fermentation is transformed into the sodium salts by treating with  $\text{Na}_2\text{CO}_3$ , and the butyric acid liberated by  $\text{H}_2\text{SO}_4$ . The butyric acid is separated by fractional distillation from acetic or capronic acids, which are usually found present in small amount. By converting the acid into the ethyl ester, fractionating this, and again regenerating the acid by hydrolysis, the chemically pure acid may be obtained. Oily liquid, with an unpleasant, rancid smell—B.P.  $162^\circ\text{C}$ .; M.P.  $-7.9^\circ\text{C}$ .; sp. gr. 0.978.

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\* 1 dz. = 100 kg. = about  $\frac{1}{10}$  ton.



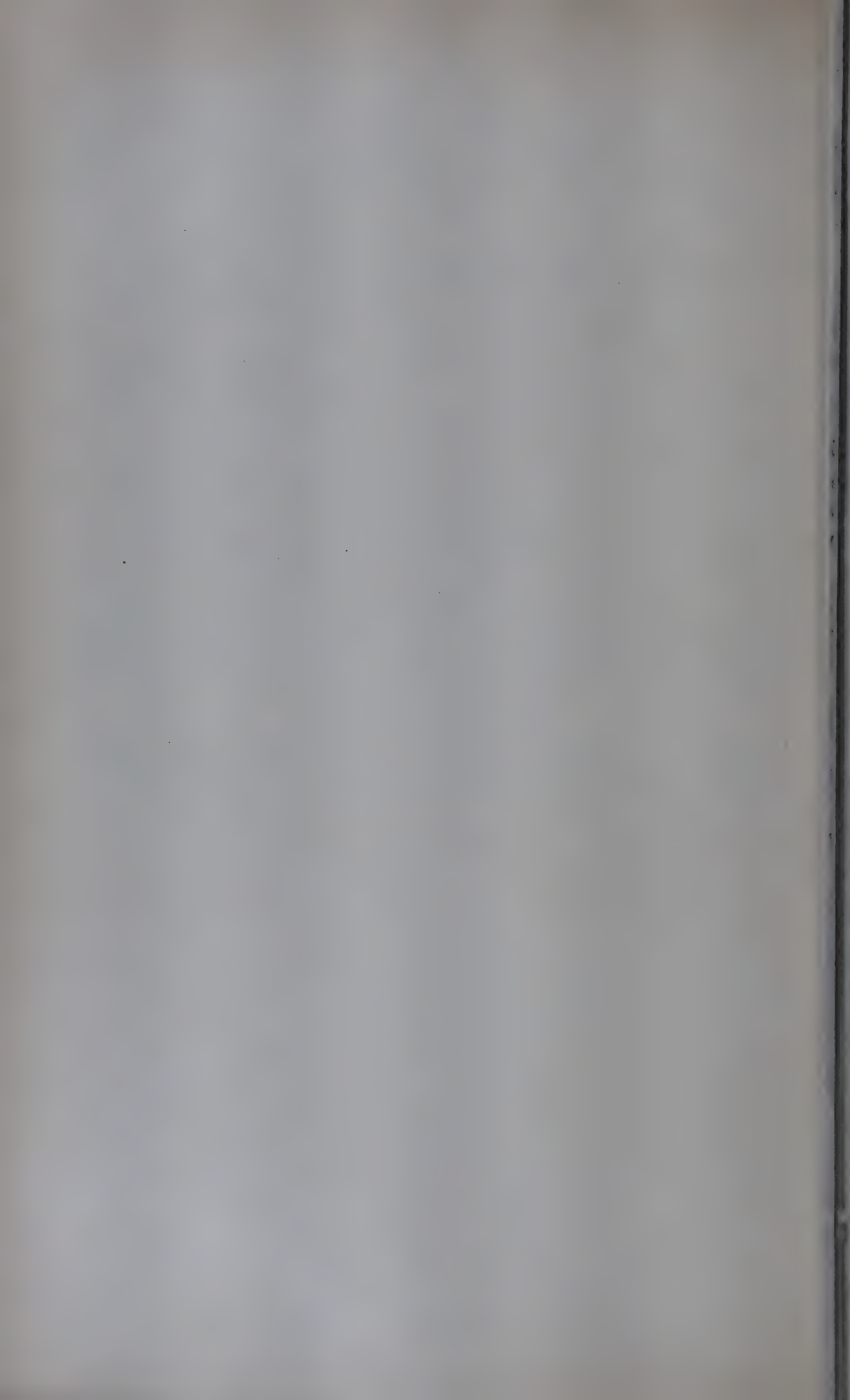
## SECTION VI

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# The Charcoal and Wood-Distilling Industries

INCLUDING THE

Manufacture of Methyl Alcohol, Acetone, and Acetic Acid





# THE CHARCOAL AND WOOD-DISTILLING INDUSTRIES

INCLUDING THE MANUFACTURE OF METHYL ALCOHOL, ACETONE, AND ACETIC ACID

By G. MARTIN, Ph.D., D.Sc.

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THE preparation of **wood charcoal** by burning wood in a supply of air insufficient for complete combustion is a very old industry which is still carried out to some extent in countries rich in wood—such as in the Harz, Steiermark, Sweden, Finland, Russia (Ural), etc., and the charcoal so obtained is much valued as a fuel, since it is free from sulphur and leaves little ash when burned. The charcoal is also used for making gunpowder, for purifying spirits, for packing in refrigerators, and for other purposes as well.

The operation is carried out in “**Meilers**” or “**Kilns**”: the wood is piled symmetrically round a central narrow shaft, and the wood is covered with a layer of charcoal, earth, and twigs. The wood is lighted in the *middle* at the bottom. A part of the wood burns, and the heat



FIG. 143.—Charcoal Kiln, with Depression on Floor for Collecting Wood Tar.

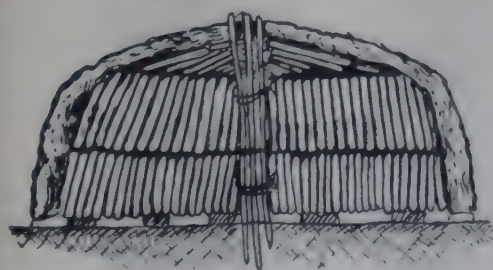


FIG. 144.—Charcoal Kiln, Ordinary Type.

thus produced reduces the rest to charcoal. The charring proceeds from the centre outwards, and the volume of the wood diminishes. Holes are finally made in the external covering in order to conduct the combustion in any required direction so that all the wood may be completely charred. The



FIG. 145.—Meyer's Large Kiln for Wood Charring, showing Appliances for Sucking off and Condensing the Vapours.



air supply must be so regulated that an actual *flame* never appears. The burning may last a week or more. 100 cub. yd. of dry wood yield 50-75 cub. yd. of charcoal. 100 parts by weight of wood containing 25 per cent. water yield 20-28 parts of charcoal containing 89-90 per cent. C, 1-2 per cent. H, 2-4 per cent. O, 2-11 per cent. water, and 3 per cent. ash.

In Sweden, Russia, and U.S. America, a considerable amount of **wood tar** is obtained by burning in this manner, or in masonry kilns. Depressions are made in the floor of the kiln under-

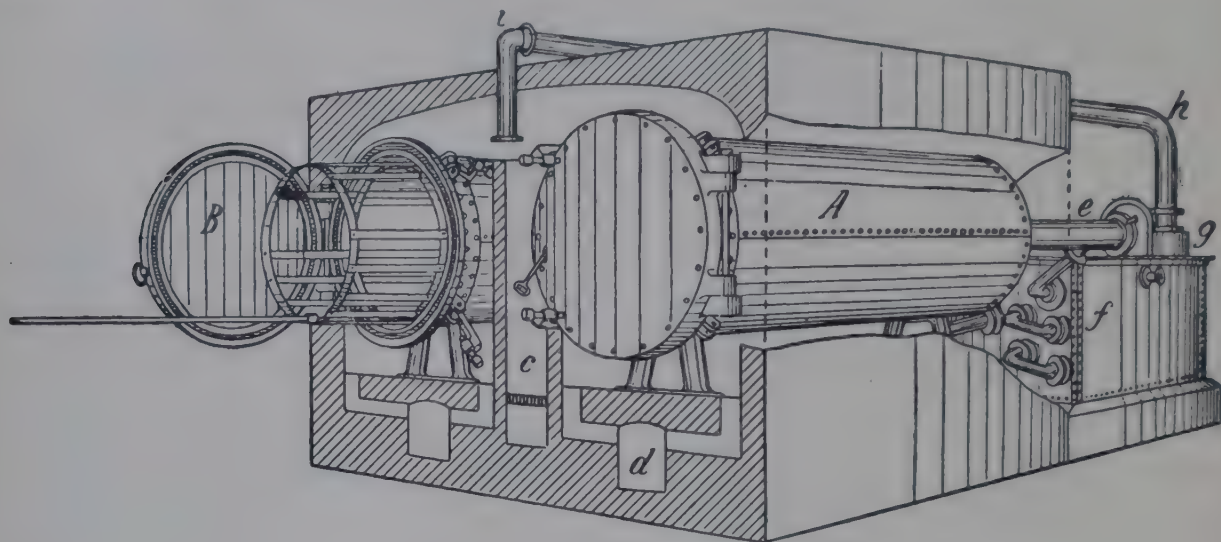


FIG. 146.—Small Retorts for Wood Distillation.

(F. H. Meyer, Hannover-Hainholz, Germany.)

neath the layer of wood (Fig. 143). The tar flowing from the heated wood into these passes out by a channel into a vessel outside the kiln, and is there collected.

Freshly made charcoal is spontaneously combustible and very hygroscopic. Its calorific value is about 7,000 calories. In this process all the valuable volatile products are completely lost.

F. H. Meyer (Hanover) has designed large kilns (Fig. 145) with appliances for sucking off vapours, and thus gaining a large yield of volatile distillates. That shown in the illustration takes 300 cub. m. of wood with a working time of twenty days.

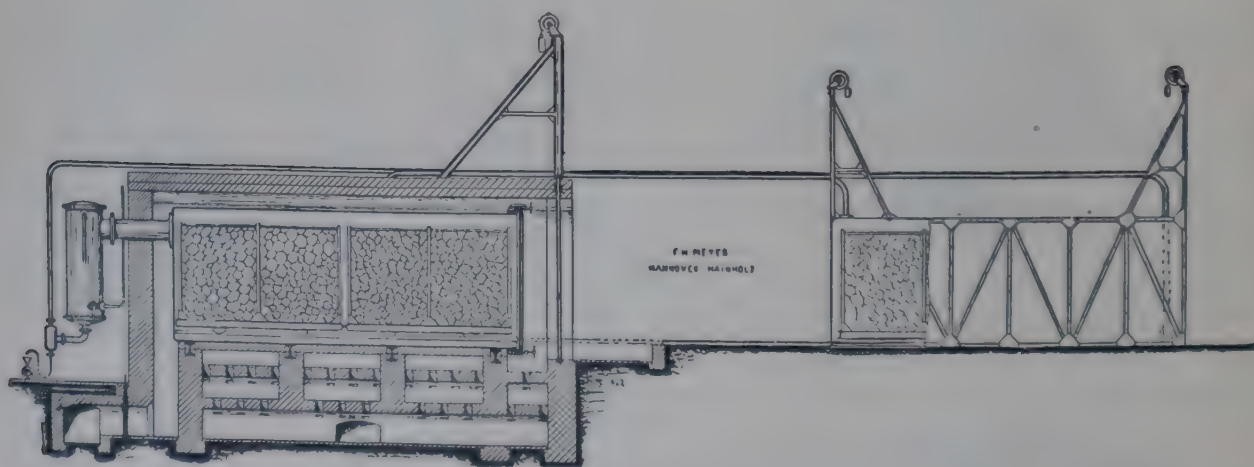


FIG. 147.—Large Horizontal Retorts for Wood Distillation, showing Wire Cage on Rails.

(F. H. Meyer, Hannover-Hainholz, Germany.)

### Destructive Distillation of Wood from Closed Retorts

The advantage of this process is that it allows the recovery of all the volatile products. The disadvantage is that the retorts are necessarily restricted in size, and consequently will not take in much wood at a time. The yield of charcoal and distillate depends very greatly both upon the nature of the wood and the manner in which the distillation is carried out. Thus if the heating be carried out rapidly in small retorts and at a high temperature, much gas and little charcoal is produced,



also little acetic acid and tar; while heating slowly in larger retorts increases the yield in oils and acetic acid and charcoal, but diminishes the yield of gas. Attaching the retorts to a vacuum pump during the process of distillation considerably increases the yield of volatile products. 100 parts air-dried wood yield on distillation:—

		Charcoal.	Tar.	Wood Vinegar.	Wood Vinegar containing Acetic Anhydride.	Gas.
Beech	{ slowly heated - - -	26.7	5.9	45.8	5.2	21.7
	{ quickly „ - - -	21.9	4.9	39.5	3.9	33.8
Oak	{ slowly heated - - -	34.7	3.7	44.5	4.1	17.2
	{ quickly „ - - -	27.7	3.2	42.0	3.4	27.0
Birch	{ slowly heated - - -	29.2	5.5	45.6	5.6	19.7
	{ quickly „ - - -	21.5	3.2	39.7	4.4	35.6
Pine	{ slowly heated - - -	30.3	4.4	41.0	2.7	24.4
	{ quickly „ - - -	24.2	9.8	42.0	2.4	24.1

Stolze obtained the following numbers as the result of slow and very careful carbonisation:—

100 lbs.	Charcoal.	Tar.	Wood Vinegar.	Wood Vinegar containing Acetic Anhydride.	Gases. Cubic Yards.
Beech - - - - -	24.6	9.5	44.0	8.9	10.8
Oak - - - - -	26.1	9.1	43	7.7	10
Birch - - - - -	24.4	8.6	44.9	8.9	9.8
Fir - - - - -	26.6	11.9	42.3	4.2	12.5

Especially worthy of remark is the small percentage of acetic anhydride in the wood vinegar from the pine and fir, and the large amount of gas yielded by fir. This explains why distillers of yellow pine seldom save the pyroligneous acid or wood vinegar.

The tar of the pine and fir contains a considerable amount of turpentine oils.

Fig. 146 shows a plant for wood distillation designed by the firm F. H. Meyer, Hannover-Hainholz. It consists of two iron cylinders A and B each about 3 m. long and 1 m. diameter embedded in masonry and heated by means of a fire *c* placed intermediately between them. The hot gas and flame from the fire circulate round the retorts and slowly char the wood. The non-condensable gases coming over with the products of distillation pass from the condenser *g* through the tube *hi* and are burned as fuel under the retorts. The temperature is initially kept as low as possible. Up to 150° C. the distillate consists principally of water; between 150°-280° C. the bulk of the acetic acid and methyl alcohol comes over; above 300° C. tar distils. The gas escaping consists at first mainly of CO<sub>2</sub>; at a higher temperature CO, CH<sub>4</sub>, and H<sub>2</sub> gas comes over. Heavy gaseous hydrocarbons are hardly produced at all as with coal. The gases burn with a pale non-luminous flame. Immediately connected with the retort is a wide tube *e* leading to a tar separator, followed by a coil of copper tubes *f*, cooled by water in a tank. Here the liquid distillate condenses and can be run off into a suitable receptacle.

The non-condensable gases from the retort first pass a hydraulic seal (as in gasworks) *g*—to prevent the flame striking back—before passing along *hi* to the furnace.

The wood, cut into pieces of a suitable length and thickness, is placed in the retort by means of a wire-work cage, which slides in and out of the retort. In larger retorts the wood is placed in wire cars mounted on wheels, which run on rails in and out of the furnace. Fig. 147, which represents a modern plant manufactured by F. H. Meyer of Hannover-Hainholz, Germany, shows the most general type of retort, which is used in large works both in America and on the Continent, and which is rapidly replacing the oven system. Sometimes a steam exhaustor is attached to the outlet from the retort, whereby the yield of acetic acid is considerably increased, since the volatile vapours are thus sucked out from the retort before they have been decomposed by the hot walls and high temperature. Dry wood gives the best results.

The distillation lasts twelve hours. The charcoal is withdrawn in closed iron-plate cylinders and is allowed to cool.



A cubic metre dry beech, weighing 396 kg., yields approximately 122 kg. charcoal, 157 kg. wood vinegar (containing 18.5 kg. acetic acid, and 4.6 kg. methyl alcohol), 24 kg. wood tar of sp. gr. 1.08, 93 kg. of gases; while to carry out the distillation needs about 43.5 kg. coal to heat the furnace.

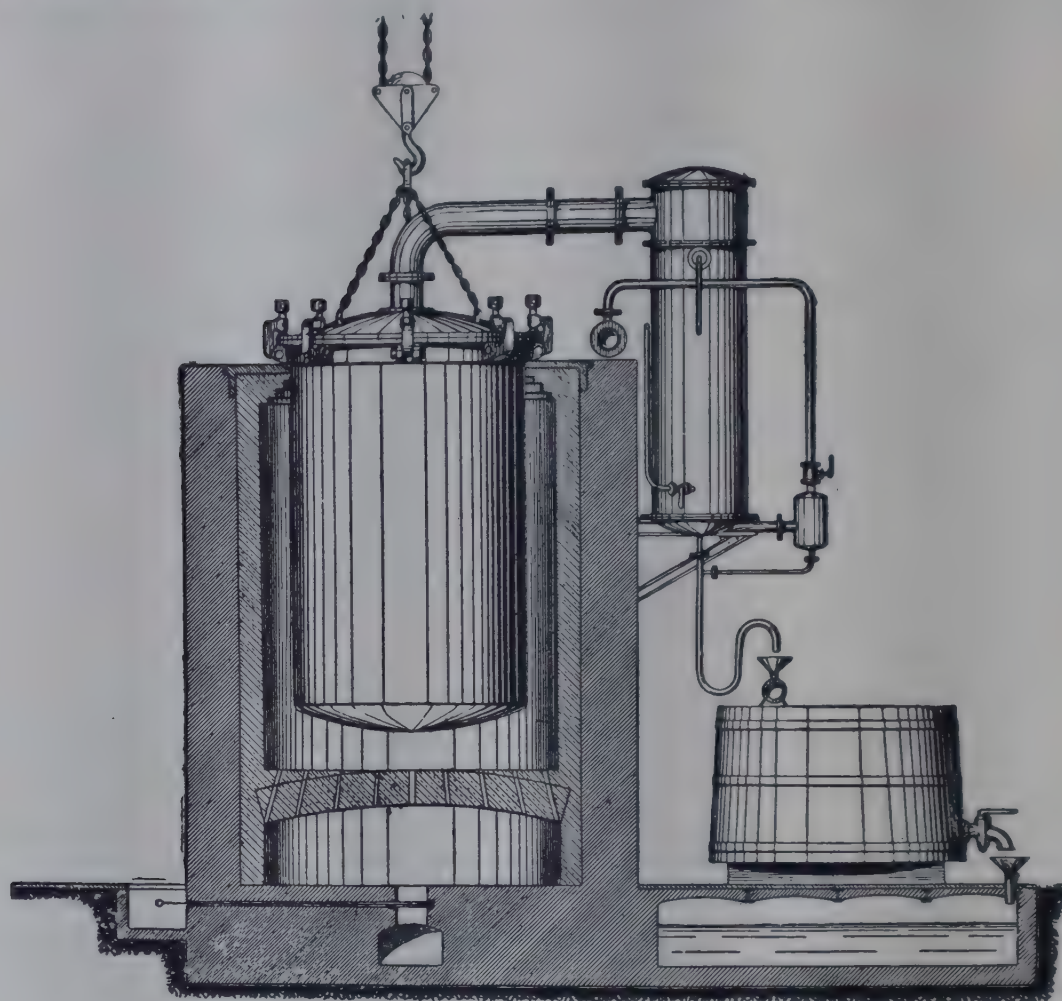


FIG. 148.—Vertical Retort.

(F. H. Meyer, Hannover-Hainholz, Germany.)

When pine wood or fir containing much resin has to be distilled, usually *vertical* retorts are employed which contain at the bottom an outlet tube for the melted resin—a rather valuable product (Figs. 148, 149). Such retorts, although yielding better charcoal, are slightly dearer to work than horizontal retorts.

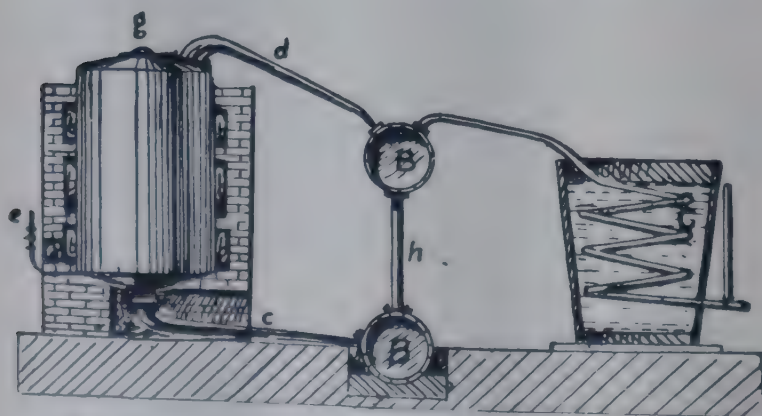


FIG. 149.—Vertical Retort for Pine Wood, showing Outlet Tube at bottom for Melted Resins.

**Gröndal's Tunnel Kiln for Charring Wood** (German Patent, 112,932, 18th July 1899).—The Iron and Steel Institute of Sweden in 1904 judged this system to be the best in use at that time; it is used at Pitkäranta in Finland. It consists of a masonry tunnel 66 m. long, divided into several compartments by dampers or doors of iron

plate. The first compartment, 4.5 m. long, is the entrance chamber. Next comes the charring chamber, 40 m. long, followed by a 17 m. long "charcoal cooling" chamber, and finishing with another "entrance chamber" 4.5 m. long. Trucks on rails loaded with wood can be drawn through the tunnel. The central



"charring chamber" is really a sort of muffle furnace, heated by the hot gases of a furnace placed beneath the tunnel, the flames pass through earthenware or iron tubes running round the interior of the chamber between the walls and the trucks, so that the temperature is kept continuously high enough to completely carbonise the wood. No gases from the fire, however, actually enter the chamber and come in contact with the wood. The volatile products from the wood escape through pipes in the roof and are condensed in the ordinary way, as in the retort system. The tar in the wood drips from the cars on to the floor of the furnace, and runs into depressions placed in the floor at intervals, thence escaping through pipes to tanks placed on the outside of the furnace.

The wood, cut up into suitable slices, is loaded into wire-cage trucks and is placed in the furnace as follows: First the outer door of the entrance chamber is opened and a truck run in—the chamber being just big enough to hold it—and the door is shut. Then all the sliding doors between the two entrance chambers are opened, and the whole row of trucks inside (filled with wood) are drawn through

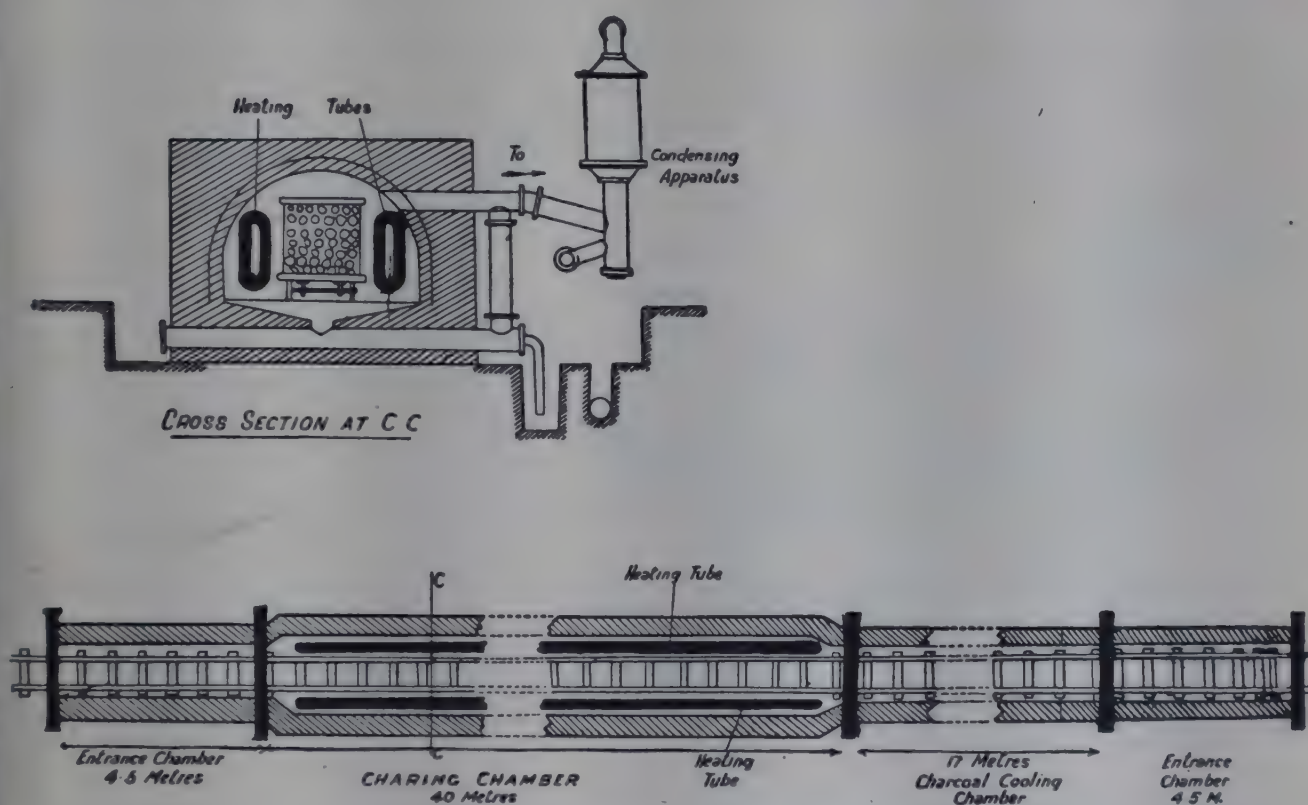


FIG. 150.—Gröndal's Tunnel Kiln for Charring Wood.

a waggon length by means of a winch placed outside the furnace. Consequently the last waggon in the furnace, which contains the charred wood or charcoal ready to be removed, is drawn into the last entrance chamber, while the fresh wood truck is drawn from the first entrance chamber into the central charring chamber. The furnace thus works, practically, continuously. Every hour a truck of wood is drawn into the furnace at one end, and simultaneously, at the other end, a truck of charcoal is withdrawn. The yield is stated to be less with this furnace than by other constructions, but it is very suitable for countries rich in wood and needing much charcoal.

### Steam Distillation of Wood before Charring

Occasionally pine or fir wood rich in turpentine or resin is steam-distilled with saturated or superheated steam *before* carbonising, in order to recover the turpentine oil. The steam from a boiler passes through a superheater, and then in succession through two or more retorts. The melted-out liquid resins flow away from the



floors of the retorts, while the distilled products pass over to a condenser. The wood is left dry—using superheated steam—and is then charred in the usual way.

Before charring the wood is sometimes extracted with solvents to recover rosin left in the wood; see under **Turpentine Industry**, p. 338.

### Distillation of Sawdust and Wood Waste

Sawdust is difficult to distil in ordinary retorts owing to the fact that it is an extraordinarily bad conductor of heat—so that the outer portions char before the internal layers are scarcely hot. Moreover, the charcoal formed is of little value since it will not form a coherent mass. Various devices are used, such as revolving iron retorts, through the interior of which flames play. Halliday's apparatus, much used in England, consists of a cylinder with a feeding screw, placed in a furnace. According to the speed with which the screw is driven, the wood can be exposed for a shorter or longer time to the action of the heat. Thus, as large as possible a yield of acetic acid is obtained (Fig. 151).

### WOOD TAR AND PYROLIGNEOUS LIQUOR

The liquor distilling over from the retorts in which the wood is being carbonised separates out into: (1) **Wood Tar**, (2) **An Aqueous Layer called Pyroligneous Liquor** (or crude wood vinegar).

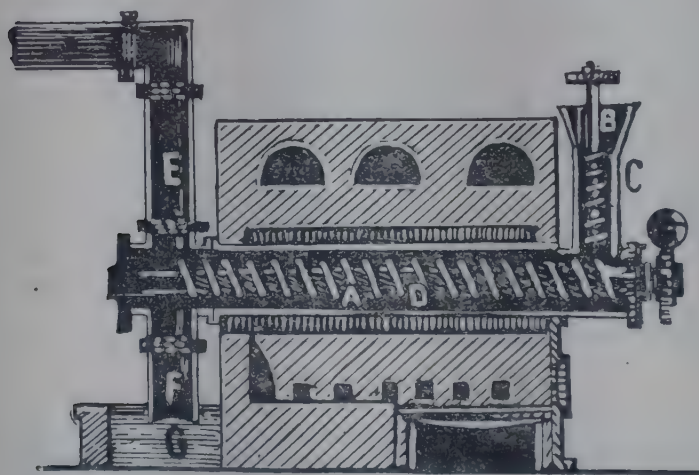


FIG. 151.—Halliday's Apparatus for Distilling Sawdust and Wood Waste.

Some very important improvements in the separation of tar from the pyroligneous acid were made by the firm F. H. Meyer, Hannover-Hainholz, in 1904 (see German Patents, Nos. 189,303 and 193,382). To effect a technically complete separation of tar from the pyroligneous liquor, they attach to the retorts a special condensing apparatus (Fig. 152). The gases from the charring retorts enter at T and pass into a chamber A which is heated to a suitable temperature by the live steam coil *c*. In A the bulk of the tar condenses together with some acetic acid. The latter, however, is again volatilised by the steam issuing from the coil *c*. The vapours—already relatively tar-free—

rise up through A and pass into a successive series of chambers through bell capsules *b*, where a further condensation of tar takes place and the vapours passing through become still richer in acetic acid. The process is repeated in the successive chambers B, C, D, E, and the vapours finally escaping from E are practically free from tar, and on condensation and neutralisation with lime, directly yield grey 82 per cent. acetate of lime. The separated tar, pouring down through the tubes *a, a, a*, runs away at the base through a special outlet.

### Wood Tar

**Treatment of the Wood Tar.**—The wood tar is run off from the aqueous layer of pyroligneous liquor and specially worked up. It contains an enormous number of substances, such as paraffins and other hydrocarbons, high boiling phenols and their esters (but only a small amount of phenol,  $C_6H_5OH$ ), such as paracresol, guaiacol,  $C_6H_4 \begin{smallmatrix} OH \\ \diagup \\ OCH_3 \end{smallmatrix}$ , kreosol,  $C_6H_3(CH_3) \begin{smallmatrix} OH \\ \diagup \\ OCH_3 \end{smallmatrix}$ , pyrogallol esters, fatty acids and esters, and pitch.

**Pine-Wood tar** contains much turpentine.

**Beechwood-Wood tar** is especially rich in guaiacol and kreosol.

The so-called "Stockholm Tar"—principally from pine wood—is much valued as a preserving paint for ships, roofing, masonry, etc.



**Distillation of Wood Tar.**—Wood tar is distilled in a manner similar to coal tar, using the same precautions against boiling over. It is then separated into **Light Tar Oils**, **Heavy Tar Oils**, and **Pitch**. The **Light Tar Oils** are used much in the same way as **Benzine**. The lighter oils from **pine tar** are known as “Pine Oil,” and are especially rich in **turpentine**; it is largely used for making paints, varnishes, and lacs. The more mobile part of **birch tar**, known as “Birch Tar Oil,” is used in finishing **Russian leather**.

The **Heavy Tar Oils** (oil of pitch) are largely used in pharmacy and for

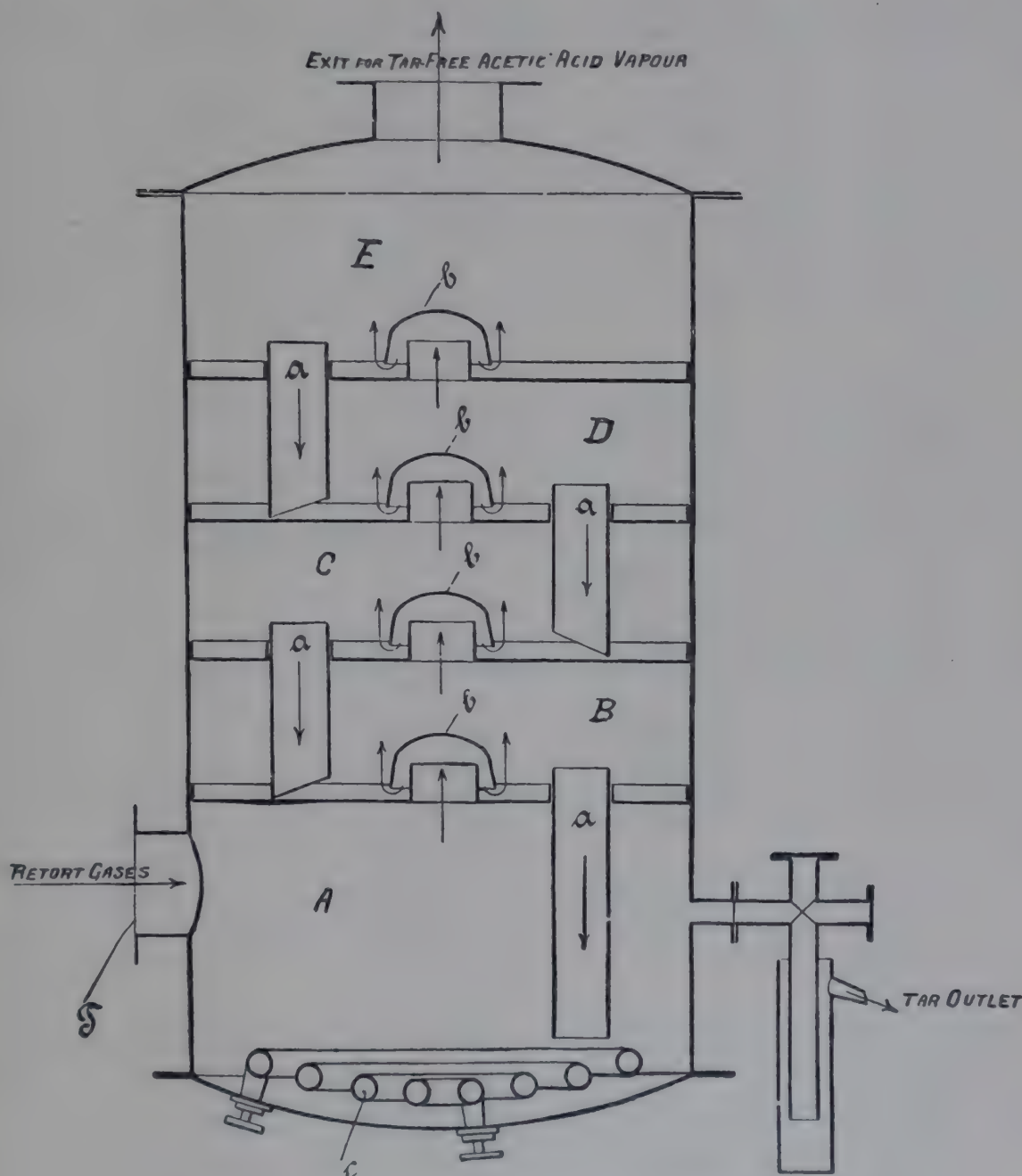


FIG. 152.—F. H. Meyer's Apparatus for Separating Tar from Pyroligneous Liquors.

impregnating wood, etc., being more suitable for the latter purpose than the corresponding oils from coal tar.

A **Creosote** is obtained from **beechwood** heavy tar oils by extracting with caustic soda solution, and precipitating with  $\text{CO}_2$  or acid.

This creosote boils between  $200^\circ\text{--}220^\circ\text{C.}$ , has a sp. gr. 1.07, and has a strong *smoky* odour. It consists principally of **guaiacol** and **kreosol**, and is used:

(1) In the “quick smoking” process for ham, fish, etc.; (2) as an antiseptic in

medicine, being considerably less poisonous than phenol; (3) in medicine, especially for coughs, colds, consumption, etc. etc. Some of the "Pine Tablets," etc., placed on the market consist largely of these substances.

Pure **Guaiacol**,  $C_6H_4(OH)(OCH_3)$  (1 : 2), isolated by means of its potassium or barium salt, is obtained in large colourless needles, B.P.  $205^\circ C$ . It is also produced synthetically, *e.g.*, by heating pyrocatechin with KOH and potassium methyl sulphate to  $180^\circ C$ .

**Wood pitch**, the residue left in the still, is mixed with coal tar or colophony asphalt, and sold for shoemaking.

**Statistics.**—England imported (principally from Russia) in 1910 about 279,600 cwt. of wood tar, of value £87,500. The United States in 1910 imported 1,018 barrels (280 lbs. to the barrel) of tar and wood pitch. For modern statistics see Appendix III.

### Pyroligneous Liquor or Crude Wood Vinegar.

The aqueous layer of pyroligneous liquor separated from the coal tar (above, p. 328) contains about 10 per cent. acetic acid, 1-2 per cent. methyl alcohol, 0.1-0.5 per cent. acetone, as well as small amounts of propionic, butyric, formic, and other acids, methyl acetate, allyl alcohol, furfural, phenols, amines, ketones, etc. Suspended or dissolved in the aqueous fluid occurs about 10 per cent. of tarry matter.

**Treatment of the Pyroligneous Liquor.**—The liquor is distilled in order to separate the acetic acid, methyl alcohol, and tarry matter. The crude wood vinegar is placed in a vessel and boiled by means of a steam coil. The distillate passes in succession into two boilers, each charged with milk of lime. Here the acetic acid is fixed by the lime forming **calcium acetate**, while the methyl alcohol, passing on, is fractionated and condensed in a still. Any methyl acetate distilling is saponified by the lime into methyl alcohol and acetic acid.

A great saving in fuel, steam, and space is effected by F. H. Meyer's system (German Patent, 193,382) of distilling the pyroligneous acid in multiple evaporators in vacuum.

**Manufacture of Acetate of Lime.**—The contents of the boilers containing excess of lime and calcium acetate (which is in solution), are run off filtered, the solution evaporated with continual stirring in steam-heated copper pans. The tarry matter rising to the surface is skimmed off through a sliding door. When the specific gravity reaches 1.116, the calcium acetate separates as a thick paste, which is removed and spread on flat iron pans to be dried, continually stirring the while with iron shovels. The "grey" acetate contains 80-82 per cent. calcium acetate and 20 per cent. water (from which it cannot be freed without decomposition).

**Uses.**—As a source of acetic acid, acetates, and acetone. Used in **Waterproofing**, p. 526.

**Statistics.**—The *export* of acetate of lime from the United States is shown by the following figures: 1906, 31,000 tons; 1910, 28,000 tons; value in 1910, \$1,423,000.

The English import of acetate of lime (almost entirely from Canada and the United States) in 1910 amounted to 4,300 tons (value £42,000). Germany produces about 10,000 tons.

### Manufacture of Concentrated or Glacial Acetic Acid

S. MIERZINSKI.—"Die Industrie der Essigsäure u. d. essigsäueren Salze." Leipzig, 1905.

Glacial acetic acid is now manufactured almost entirely from the crude grey calcium acetate obtained from wood distillation plant (see above).

The method adopted is to decompose the calcium acetate with concentrated sulphuric acid, when acetic acid of 70-75 per cent. distils over mixed with  $SO_2$  and other gases. 100 parts 80 per cent. calcium acetate are placed in cast-iron boiler provided with powerful stirring apparatus and heated by steam. About 60 parts



of 66 per cent. sulphuric acid are slowly run in and the distillation carried out in a vacuum (see Lindes' German Patent, 92,418, 29th November 1894). The acetic acid distilling over is condensed in copper or earthenware tubes, while non-condensable evil-smelling gases pass on and are led into the furnace. A considerable amount of  $\text{SO}_2$  escapes while part remains dissolved in the acetic acid. A mass of calcium sulphate mixed with charred carbonaceous matter remains in the boiler. The crude 70-75 per cent. acetic acid thus obtained (containing 0.1 per cent.  $\text{SO}_2$ ) is then fractionated from copper (or chamotte-plated cast-iron) boilers, using a columnar condenser as in spirit distillation.

The still is heated with steam and is coated internally with chamotte plates (since acetic acid in the presence of air attacks copper). The vapours pass out into a rectifying column, usually constructed entirely out of porcelain or other acid-fast material, the outer casing being, however, of copper. In a water tank at the top of the rectifying column lies the **dephlegmator** (see under **Spirit Distillation**), which dephlegmates the dilute acid coming over at first. Later, when the pure acetic acid distils, the dephlegmator is disconnected. The first runnings consist of dilute acetic acid containing  $\text{SO}_2$ , then the bulk of the practically pure acetic acid distils over, followed finally by heavier homologous acids, such as **propionic** and **butyric** acid. The glacial acetic acid is finally purified by adding potassium permanganate and rectifying, using silver condensing coils.

The *Chem. Fabrik Rhenania* (German Patent, 117,539, 8th March 1898) obtains a very pure 90 per cent. acid by decomposing calcium acetate by means of sodium polysulphate,  $\text{NaH}_3(\text{SO}_4)_2$  (obtained as a by-product in manufacturing nitric acid, German Patent, 106,962, 8th March 1898), using a reflux condenser, when the reaction—



takes place. The product is free from  $\text{H}_2\text{SO}_4$  and  $\text{SO}_2$ , and needs only rectifying once.

*E. A. & J. Behrens* (German Patent, 121,199, 6th October 1899) dissolve the commercial 82 per cent. dry calcium acetate in 60 per cent. acetic acid, and add the theoretical amount of 92 per cent.  $\text{H}_2\text{SO}_4$ . The  $\text{CaSO}_4$  precipitating abstracts the water from the acetic acid ( $\text{CaSO}_4 + 2\text{H}_2\text{O} = \text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ), and the whole mass becomes solid, when the concentrated acetic acid is pressed over in the cold, or simply distilled.

**Properties.**—Pure 100 per cent. glacial acetic acid melts at  $17^\circ \text{C}$ ., boils at  $118^\circ \text{C}$ .; technical glacial acetic acid contains 96-99 per cent. of acid. The pure acid should not decolourise potassium permanganate. On diluting with water the specific gravity *increases*, attaining a maximum density with an 80 per cent. acid; thereafter it diminishes, as the following table shows:—

Acetic Acid, Weight per Cent.	Sp. Gr. $15\frac{1}{4}^\circ \text{C}$ .	Acetic Acid, Weight per Cent.	Sp. Gr. $15\frac{1}{4}^\circ \text{C}$ .
100	1.0553	40	1.0523
90	1.0713	30	1.0412
80	1.0748	20	1.0284
70	1.0733	10	1.0142
60	1.0685	0	0.9992
50	1.0615		

**Statistics.**—Germany produces about 10,000 tons (at 550 m.) annually, 3,000 tons of which go in the manufacture of synthetic indigo (see this). England in 1910 imported 4,500 tons (value, £88,000). For modern statistics see Appendix III.

**Uses.**—Largely used in coal-tar colour manufacture. The manufacture of synthetic indigo alone uses up over 3,000 tons yearly. The preparation of mordants—such as aluminium acetate, iron acetate, chromium acetate, copper acetate—for the cloth-dyeing and printing trades uses up very large amounts of acetic acid. The great value of acetate mordants lies in the fact that the acid is volatile, and on steaming escapes, leaving behind the sesquioxides of the metals. They are usually produced in solution in the dye vats by decomposing lead or calcium acetate with the sulphates of the required metals, the lead or calcium being precipitated as sulphate.

Crude acetic acid is used for smoking meat and fish. Pure acetic acid from wood is also used largely in Germany and France as a **table vinegar**, being flavoured for the purpose by digesting with certain aromatic herbs, such as fennel, being sold in a 70 per cent. solution as "Essence of Vinegar." See also **Vinegar**, p. 317.

#### Salts

**Lead Acetate**, "Sugar of Lead,"  $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 3\text{H}_2\text{O}$ , is obtained by dissolving litharge,  $\text{PbO}$ , in crude acetic acid or vinegar. The aqueous solution takes up more lead oxide forming basic acetates. Crystallises well.



**Calcium Acetate**,  $\text{Ca}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot \text{H}_2\text{O}$ , is an easily soluble body, but forms crystals with difficulty (see p. 330).

**Sodium Acetate**,  $\text{Na}(\text{C}_2\text{H}_3\text{O}_2) \cdot 3\text{H}_2\text{O}$ , forms an easily soluble crystalline salt.

**Copper Acetate** (Verdigris),  $\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot \text{H}_2\text{O}$ , used as a paint (see **Pigments**).

**Iron Acetate solution** is obtained by dissolving scrap iron in crude acetic acid. Used as a mordant.

For **Esters** of acetic acid see under **Alcohol Preparations**.

**Monochloroacetic acid**,  $\text{CH}_2\text{Cl} \cdot \text{COOH}$ , M.P.  $62^\circ$ , is now prepared on a very large scale for the manufacture of synthetic indigo, by passing chlorine through hot glacial acetic acid in the presence of acetic anhydride.

### Methyl Alcohol, Wood Spirit

The crude methyl alcohol collected during the distillation of the pyroligneous liquid (see p. 330) contains about 10 per cent. methyl alcohol. It is rectified over milk of lime in a columnar still, and is thus placed on the market as 80 per cent. "Crude Wood Spirit"; this contains as impurities allyl alcohol, acetaldehyde, formaldehyde, furfurol, methylethylketone, acetone, amines, pyridine, etc.

It is purified by diluting to 30-40 per cent., adding milk of lime (20-30 l. to every 1,000 l. of spirit), and carefully and slowly rectifying from large columnar stills for several days. The first runnings contain 8-60 per cent. acetone, and some allyl alcohol; while the final fractions contain high boiling ketones, and are known as "wood oil"—a practically valueless by-product. The intermediate fractions consist of nearly pure methyl alcohol, which is obtained practically pure by again diluting with water, adding some  $\text{NaOH}$ , and rectifying. Last traces of acetone may be removed by distilling over bleaching powder, which converts the acetone into chloroform, but at the same time destroys some of the methyl alcohol. Dark-coloured, sharp-smelling impurities are often removed by filtering through wood charcoal.

**Properties.**—Pure methyl alcohol,  $\text{CH}_3\text{OH}$ , boils at  $66^\circ \text{C.}$ , has sp. gr. 0.80, and has a faint, spirituous odour. Taken internally it intoxicates, but is too dear for use as a spirituous liquor.

**Uses.**—Pure acetone-free methyl alcohol is much used in the colour industry for making dimethylaniline, methyl chloride,  $\text{CH}_3\text{Cl}$ , methyl bromide,  $\text{CH}_3\text{Br}$ , and

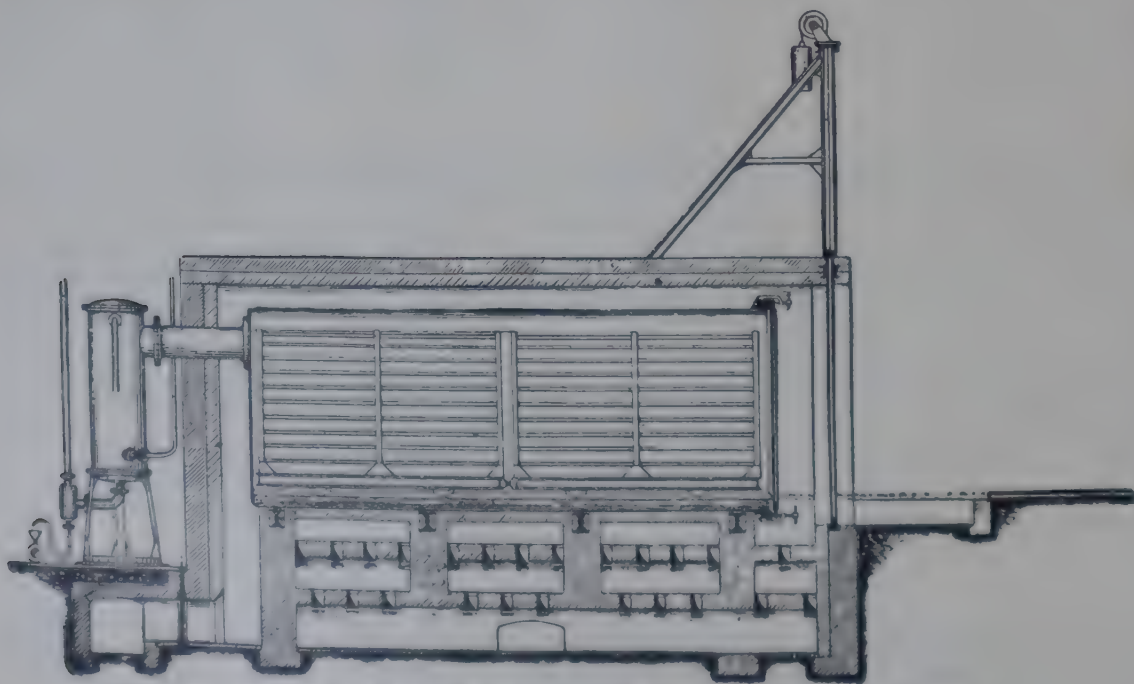


FIG. 153. — F. H. Meyer's Apparatus for Manufacturing Acetone.



other methyl compounds. Crude wood spirit containing acetone and other impurities has a sharp, aromatic smell and taste, and is used for denaturing alcohol (thus producing "Methylated Spirits") as well as for varnish making, French polishing, etc.

The source of methyl alcohol is invariably **wood**. The amount of acetone it contains is determined by the **Iodoform Test**. (See **Acetone**.)

**Statistics.**—Germany in 1905 imported 4,770 tons at 700 m. from North America and Austria. England in 1910 imported 448,500 gals. (value, £47,000), of which no less than 400,000 gals. came from the United States. The *export* of wood alcohol from the United States is shown by the following figures: 1906, 780,000 gals.; 1907, 2,150,000 gals.; 1908, 1,959,000 gals.; 1909, 1,100,000 gals.; 1910, 1,329,000 gals.; value in 1910, \$582,000.

For modern statistics see Appendix III.

**Acetone, Dimethylketone**,  $\text{CH}_3\cdot\text{CO}\cdot\text{CH}_3$ , is a clear, mobile, ethereal-smelling liquid, boiling at  $56.5^\circ\text{C}$ ., and of sp. gr. 0.797 at  $15^\circ\text{C}$ . Although it occurs in crude wood spirit it is seldom isolated from it, being used in the impure state for denaturing alcohol. Pure acetone is manufactured on F. H. Meyer's system by heating crude calcium acetate to  $300^\circ\text{--}400^\circ$  in perforated trucks placed in a retort (Fig. 153):— $\text{Ca}(\text{CH}_3\cdot\text{COO})_2 = (\text{CH}_3)_2\text{CO} + \text{CaCO}_3$ . The volatile acetone vapours escape through a pipe and are condensed. There remains in the truck finely powdered  $\text{CaCO}_3$ , which is removed by opening the retort and running out the truck. The crude acetone contains homologous acetones and acids, as well as aldehyde, while  $\text{CH}_4$  escapes. The acetone is purified by fractionating over lime. 100 kg. of 80 per cent. calcium acetate yield 25-30 kg. crude acetone of 60-70 per cent. Tralles. 100 parts of wood yield about 1 part of acetone.

Up to 1912 the sole source of acetone was the dry distillation of wood and the subsequent decomposition of calcium acetate. Owing to the modern use of wood pulp for paper, and the consequent diminution in the supply of wood available for destructive distillation, coupled with the low yield of acetone (only 1 per cent. of the weight of the wood), the supply of acetone was not meeting the rapidly increasing demand, and so the price had been rising until in 1912 it reached £89 per ton. In that year *A. Fernbach* introduced his **Fermentation Process** for producing acetone from starch. Grain, potato, or other starchy mashings are inoculated with Fernbach's culture, and allowed to ferment. The starch breaks down into higher alcohols (principally butyl) and ketones, of which acetone forms a considerable portion. The mashings are then distilled, and the acetone separated by fractional distillation. It is found that 15-20 per cent. of the starch is transformed into acetone. The crude starch acetone contained 78 per cent. pure acetone, 11 per cent. of "Miscible Ketones," and 11 per cent. impure acetone. The Synthetic Products Company of London placed the acetone on the market by this process at £35-£45 per ton (see p. 314).

**Uses of Acetone.**—Acetone is a valuable product employed for making chloroform (p. 378), iodoform (p. 380), and as a solvent for acetylene (pp. 401, 403); in making celluloid (p. 208), and synthetic drugs (p. 605). By far the greater quantity, however, is employed as a solvent for nitrocellulose in the manufacture of blasting materials and smokeless powders, such as cordite (see p. 639).

Acetone is also manufactured catalytically by pressing acetic acid vapour over heated pumice stone or other catalyst.

For explosive manufacture the acetone must be free from all acid or aldehyde, boil at the correct temperature, and yield with iodine and caustic soda solution the correct amount of **iodoform**, according to the equation:—



Acetone (1 molecule).

Iodoform  
(1 molecule).

**Statistics.**—The English import of acetone in 1910 amounted to 22,000 cwt., of value £57,000. The world's supply of acetone in 1912 was estimated at 10,000 tons.

For modern statistics see Appendix III.





## SECTION VII

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### The Turpentine and Rosin Industry





# THE TURPENTINE AND ROSIN INDUSTRY

By G. MARTIN, Ph.D., D.Sc.

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**OIL of Turpentine, or Spirits of Turpentine**, is derived from coniferous trees, especially from the pine, *Pinus palustris*, and *P. Taeda*, L., and from the Scotch fir, *P. sylvestris*, L. Incisions are made in the bark of the trees, and the exuding viscid liquid is caught in vessels placed beneath the cut. The substance is then vacuum distilled in a current of steam. The volatile turpentine oils (forming about 17 per cent. of the mass) distil over and are collected. There remains in the boiler the non-volatile colophony, which is run off. A modern plant is shown in the diagram, Fig. 154.

The crude resin is placed in a receptacle provided with a wire-net filter. It is melted by means of heat supplied by steam passing through the double bottom with which the receptacle is provided. Simultaneously a vacuum is set up in the still A by means of a vacuum pump. The melted resin is then strained through the wire netting and enters the still A through *a*. Here, under a vacuum of 15-25 cm. and at a temperature of 175°-185° C., the volatile oils distil over. The still may be placed over a fire, but is shielded from its direct action. It is often heated by gas or merely by superheated steam.

A steam coil *cc* containing superheated steam maintains the contents in ebullition, while at the same time a current of superheated steam is driven by means of the injector *mn* through the boiling oil. The volatile distillate condenses in the copper coils immersed in the water tank *c*, and runs into the collecting tank *D*, which is connected with the evacuating apparatus; as *D* fills the liquid is run off into another reservoir. When the distillation is finished the fluid colophony is run off from the still A and allowed to solidify in suitable receptacles.

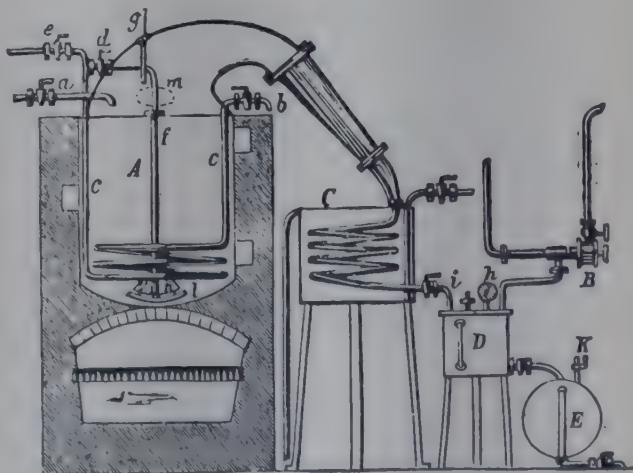


FIG. 154.—Krämer & Flammer's Vacuum Still for Rosin.

The various turpentine oils consist of a number of isomeric **hydrocarbons**, Pinene,  $C_{10}H_{16}$ ; B.P. 155°-160° C., and of sp. gr. 0.85-0.87. The various brands are distinguished by their different degrees of optical activity. The three commercial grades are important:—

1. **French Turpentine**, consisting principally of the terpene "terebenthene or laevopinene," which is *laevo-rotatory* to polarised light.



2. **American or English Turpentine** contains the terpene, **Australene**,  $C_{10}H_{16}$ , which, as regards specific gravity, boiling point, and chemical properties, strongly resembles terebenthene, but is *dextro-rotatory*.

3. **Russian Turpentine**, which contains the terpene sylvestrine and another pinene (see under **Essential Oils**).

The oil of turpentine, after distilling, is washed with caustic soda solution to retain any rosin acids. It is then redistilled and sold as "rectified spirits of turpentine." It then forms a water-white, mobile, light refracting liquid, of sp. gr. 0.640-0.872, distilling between  $156^{\circ}$ - $170^{\circ}$  C. Exposed to air it absorbs oxygen and becomes resinous.

Much turpentine is made in Russia by the destructive distillation of twigs and leaves. Turpentine being such an extremely important body, repeated efforts have been made to extract it from twigs, branches, and felled timber by various processes, such as superheated steam or solvents. One of the most promising processes is that in which the wood is heated to  $325^{\circ}$ - $375^{\circ}$  F. in a bath of rosin, washed pine tar, pine oil, soft pitch, or the heavy residuum remaining after the distillation of the lighter oils obtained from wood. The solvent extracts the turpentine and similar products from the wood, and is then drawn off from it and superheated steam is then blown through the hot rosin bath, thereby distilling over the turpentine oils. Wood so treated is especially useful for making creosoted timber or street paving blocks. Many modifications of the process are known. For some recent patents see English Patents, Nos. 4,355, 1903; 15,338, 1906; 6,831, 1907; 5,978, 1909; 19,109, 1909; 29,886, 1909; 27,076, 1910. See also pp. 327-328.

A great improvement in the rosin industry was effected by G. Walker in 1905. The turpentine is first extracted by grinding the wood and submitting it to the action of live steam in closed vessels, whereby the turpentine oil is carried over by the steam into a condenser and afterwards is refined and sold as wood turpentine. Next the wood is treated in a kind of Soxhlet extractor for the recovery of the rosin still in the wood. In an apparatus erected by Walker at Conway, S. Carolina, about 200 barrels of rosin are produced per week, together with much turpentine. The process produces five times as much rosin and turpentine in twelve hours as the same quantity of wood produces in four years by the old method of boxing the trees, and so will probably supersede the older methods.\*

**Turpentine** is one of the best and most widely used solvents for resins and oils in making varnishes and paints. The disinfectant **Sanitas** is stated to be made by passing a current of air through **Russian turpentine** in the presence of warm water.

**Turpentine Substitutes** (communicated by Mr Dancaster, B.Sc.).—The chief turpentine substitutes are rosin spirit, shale spirit, petroleum spirit, and coal-tar naphtha. All these may be used as adulterants of real turpentine or as substitutes for the latter. Also the cheaper kinds are used to adulterate the dearer. These substitutes are frequently sold under fancy names such as "turpentine," and "turpenteen." For **Rosin Spirit**, see below. For **Shale Spirit**, see p. 8. For **Petroleum Spirit**, see p. 7. For **Coal-Tar Naphtha**, see p. 417.

**Rosin or Colophony**, the residue left in the still after the turpentine oil has been removed, is one of the cheapest resins (see p. 349), occurring as a yellowish or brown brittle mass. It consists of a mixture of modifications of the anhydride of **abietic acid**,†  $C_{20}H_{40}O_2$ . It is extensively used for making varnishes, soap, rosin oils, and for sizing paper, cotton, etc. It is stable at  $150^{\circ}$  C., but between  $250^{\circ}$ - $300^{\circ}$  C. it begins to distil, yielding **rosin spirit** and **rosin oils** (which see).

The constants of rosin vary greatly with its source and quality; neutralisation value, 140-164; saponification value, 147-176; iod. value, 90-180.

**Destructive Distillation of Rosin**.—By carrying the distillation of rosin or colophony further than is required to separate turpentine oil, it is decomposed between  $250^{\circ}$ - $300^{\circ}$  C., yielding a number of oils.

The colophony is placed in a large iron still, capable of holding 50-70 barrels of rosin, and heated by direct fire. The still is connected with a suitable copper condenser and the operation takes about twenty-four hours. There finally remains in the still a coal-like mass. During the destructive distillation a considerable quantity of gas is evolved, which is led into the furnaces and burnt as fuel under the still.

\* See Pritchard, "Recent Developments in Wood Distillation," *Journ. Soc. Chem. Ind.*, 1912 418.

† The formula of abietic acid is variously given by different writers. A common formula is  $C_{44}H_{64}O_8$ .



The first distillate is a pale yellow oil, known as **rosin spirit**, boiling between  $78^{\circ}$ - $250^{\circ}$  C., and consisting of a complex mixture of hydrocarbons and oxygenated bodies, and somewhat resembling turpentine, for which it is sometimes substituted.

The distillate is washed with sulphuric acid to remove alkaline impurities, and then with caustic soda to remove acid impurities. It is then redistilled. Refined rosin spirit is a colourless, light, volatile liquid of unpleasant odour. Its specific gravity varies from 0.876-0.883. On exposure to the air it evaporates, but a portion oxidises to a resinous solid, in the same manner, but to a lesser extent, as turpentine. The spirit consists of principally various hydrocarbons, among which amylene,  $C_5H_{10}$ , hexylene,  $C_6H_{12}$ , and heptene,  $C_7H_{14}$ , have been found. When of good quality rosin spirit is the best substitute known for turpentine. Its composition, however—and therefore its quality—is very variable, and it frequently contains rosin oil, which prevents the proper drying of the paint with which it is used. It is sometimes adulterated with shale or petroleum spirit.

**Rosin Oil**, produced by the destructive distillation of rosin, comprises the bulk of the distillate; B.P.  $300^{\circ}$ - $400^{\circ}$  C.; sp. gr. 0.982-0.988; iodine value,  $112^{\circ}$ - $115^{\circ}$ . Probably consists of a mixture of **abietic acid**,  $C_{20}H_{40}O_2$ , phenols, and complex hydrocarbons,  $(C_{10}H_{16})_n$ , boiling above  $360^{\circ}$  C. Rosin oil is used as an adulterant for olive oil, boiled linseed oil, etc., also as a lubricant for iron bearings. It unites with alkalis to form greasy bodies, the compound with lime,  $(13C_{10}H_{16}).Ca(OH)_2$ , being the commercial "Rosin Grease."

**Resin Oil** is a pale yellow oil obtained after the turpentine is removed from the crude turpentine obtained by distilling wood; B.P.  $200^{\circ}$ - $214^{\circ}$ . According to Harper ["Utilisation of Wood Waste," p. 127 (1907)] it consists principally of turpineol,  $C_{10}H_{17}OH$ .

**Statistics of the Turpentine Industry.**—The English import of turpentine oil in 1910 was 23,600 tons (value, £1,000,000). Of this quantity 18,000 tons came from U.S.A. The import of rosin was 75,000 tons (value, £880,582). The United States of America produce yearly nearly £4,000,000 of turpentine oil and colophony. In 1905 Germany imported 26,200 tons of oil of turpentine and rosin oils (value, £1,000,000) and 73,540 tons of rosin (value £500,000).

The following figures show the magnitude of the United States *export*:—

	1906.	1910.	Value in 1910.
Rosin - - - - -	2,439,000 barrels *	2,144,000 barrels*	\$9,753,000
Tar, turpentine, and pitch	...	40,000 ,,	148,000
Spirits of turpentine -	15,981,000 gals.	15,588,000 gals.	8,780,000

**Acknowledgment.**—My best thanks are due to Mr W. H. Stephens, A.R.C.S., for much information regarding recent processes for extracting turpentine; also to Mr Dancaster, B.Sc., for information regarding turpentine substitutes, rosin spirit, shale spirit, etc.

For modern statistics see Appendix III.

\* 280 lbs. to the barrel.

## APPENDIX

## NATURAL AND SYNTHETIC CAMPHOR

BY G. MARTIN, Ph.D., D.Sc.

With slight additions by E. I. Cooke, M.A., B.Sc., A.R.I.C.

## LITERATURE

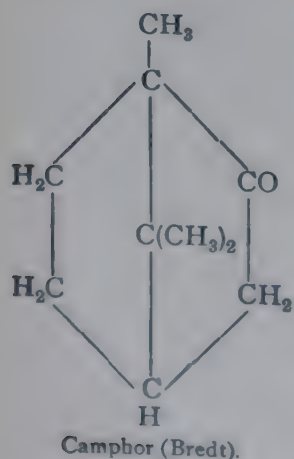
For Patent Literature relating to Camphor, see Winther's "Patente der Organischen Chemie." 3 vols. 1877-1905.

**Camphor**,  $C_{10}H_{16}O$ , is contained in the ethereal oil of the camphor tree, *Laurus camphora*, of China and Japan. It is obtained by boiling the finely divided wood with water, when the camphor floats to the surface, and on cooling solidifies. Sometimes the wood is steam-distilled. It is refined by mixing with carbon and quicklime and subliming.

**Properties.**—White crystalline solid, characteristic odour, burning taste, almost insoluble in  $H_2O$ , readily soluble in alcohol, ether, chloroform, etc. Sp. gr. 0.922-0.995; M.P.  $175^\circ$ ; B.P.  $204^\circ$ . Tough, but may be easily powdered with alcohol. Camphor is dextro-rotatory as it contains two asymmetric carbon atoms.  $[\alpha]_D = +44.2^\circ$  in alcohol.

**Isoborneol**, or **Borneol** (Borneo, Sumatra camphor), is allied to camphor, and may be converted into it by oxidation (see below).

**Uses of Camphor.**—Principally for making celluloid (which see), also in Medicine, as a moth-preventative, in fireworks and night-lights.



**Synthetic Camphor.**—Since Bredt established the constitution of camphor, numerous attempts have been made to produce it synthetically, and with considerable success.

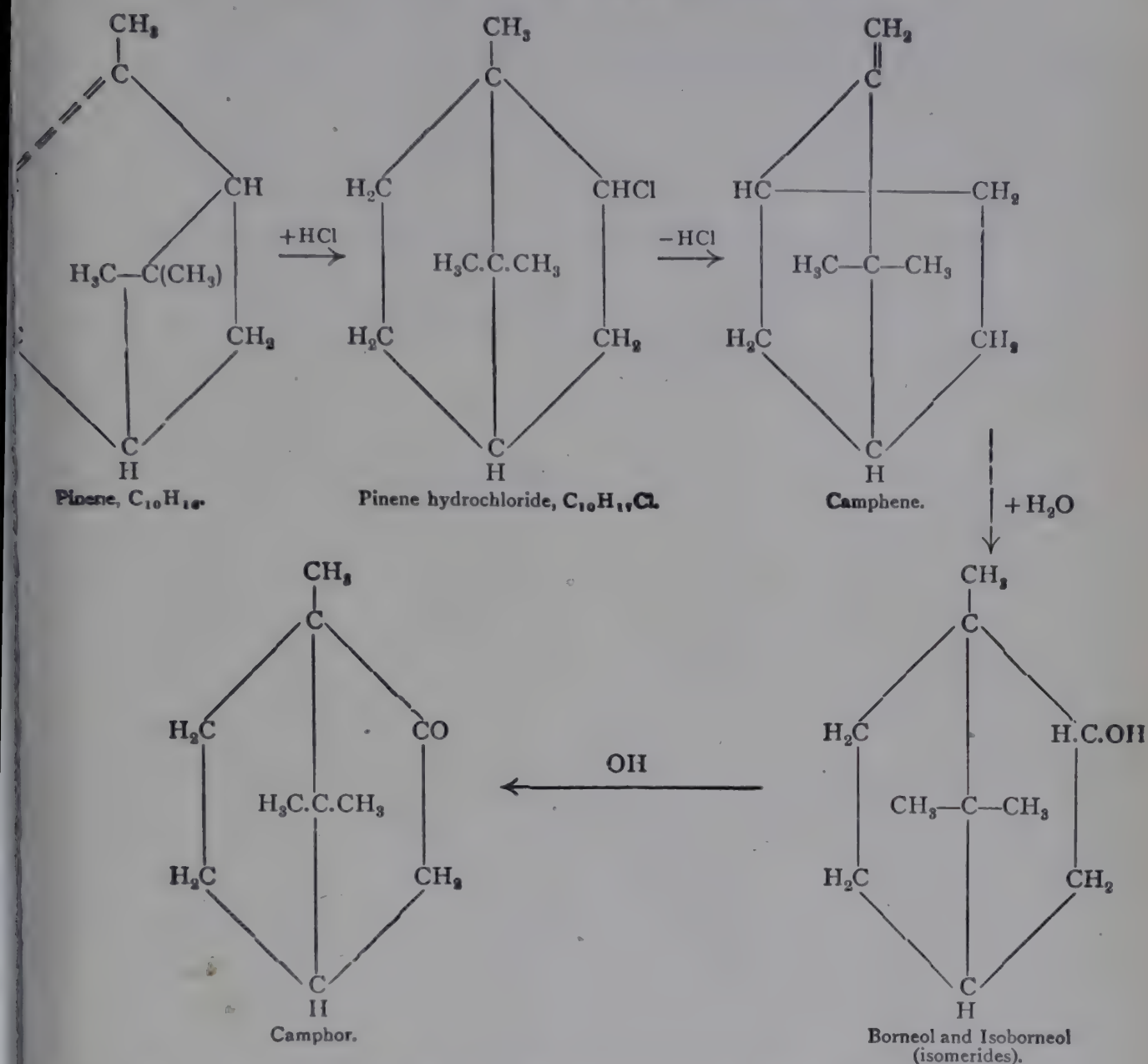
The starting point is **pinene**,  $C_{10}H_{16}$ , a terpene hydrocarbon, which may be obtained pure by the fractional distillation of turpentine oil.

Two main types of process for synthetic camphor manufacture exist, viz., those which proceed by converting **pinene** into a HCl derivative, and those which treat pinene with organic acids.

1. Dry HCl gas is led into dry pinene, and the white solid product pinenehydrochloride,  $C_{10}H_{17}Cl$ , is isolated. The Cl atom is removed by heating with alkaline reagents, when a hydrocarbon,  $C_{10}H_{16}$ , camphene, is obtained. This when treated with the lower fatty acids + a little HCl, forms an ester of isoborneol and also (a little) of borneol,  $C_{10}H_{18}O$ . Next the isoborneol and borneol is obtained from the ester by saponifying, and converted into camphor by gentle oxidation. The yield of camphor from solid pinenehydrochloride may amount to 95 per cent. of the theory.



The following scheme shows the main chemical changes which take place:—



The literature dealing with the chemical changes involved is enormous, and the number of processes patented for carrying out the various stages is very large.

The first firm to manufacture synthetical camphor was the *Chemische Fabrik auf Aktien* (vorm. Schering) of Berlin, who possess a whole series of patents. Other firms are following suit. Among the more important recent patents we may mention German Patents, 149,791, 153,924, 154,107, 185,042 and French Patent, 349,896, 1904, which deal with the conversion of pinenehydrochloride into camphene. The German Patent, 67,255 (expired 1901), of Bertram (conversion of camphene into the ester of isoborneols and borneols by heating with acetic acid + a little concentrated H<sub>2</sub>SO<sub>4</sub> below 50° C. and saponifying resulting ester with production of borneol and isoborneol) is the most important one for the production of borneol and isoborneol from camphene. Other patents are German Patent, 178,934 (uses fatty acid salts or aromatic carboxy acids instead of acetic acid), English Patent, 5,549, 1904, and French Patent, 349,852, (1904), convert pinenehydrochloride direct into borneol and isoborneol by heating it for ten hours at 120° in an autoclave with an alcoholic solution of NaOH + Na formate.

The oxidation of borneol and isoborneol is covered by numerous patents, such usual agents as air, oxygen, ozone, chlorine, nitric acid, KMnO<sub>4</sub>, etc. etc., being used. By treating camphene with ozone, Richardson (English Patent, 3,555, 1896) and Nordheim (German Patent, 64,180) convert camphene directly into camphor with a yield of 80 per cent. theory.

2. **Pinene** (or turpentine oil) is heated at 100° C. for thirty-six hours with acetic acid, when borneol acetate is obtained (see Bouchardat and Lafont, *Comp. rend.* (1886), 102, 171). This on saponifying yields borneol and isoborneol, which are then converted into camphor by oxidation as before.

The yield is bad by this method : such products as limonene, dipentene, and others are generated from the pinene. Hence, although the method is extraordinarily simple, the methods comprised under (1) still hold the field. Repeated attempts have been made to improve the yield ; for example, the German Patents, 175,097, 178,934 (Chemische Fabrik von Heyden), use salicylic acid instead of acetic, for heating with pinene ; anhydrous oxalic acid is proposed in the American Patent, 698,761, and German Patent, 134,553—the yield amounting to 35 per cent. theory.

The camphor monopoly, which the Japanese Government established after the annexation of Formosa, has been broken down by the manufacture of synthetic camphor.

Camphor is now produced catalytically by heating oil of turpentine in the presence of borophosphoric acid, magnesium, or nickel sulphate.

**Statistics.**—The United States in 1910 imported 3,027,000 lbs. (value \$922,000) of crude camphor, and 477,000 lbs. (value \$180,000) of refined or synthetic camphor.

For modern statistics see Appendix III.

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SECTION VIII

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Industrial Gums and Resins





# INDUSTRIAL GUMS AND RESINS

BY J. NEWTON FRIEND, D.Sc., Ph.D

## LITERATURE

For Rosin (Colophony) see under *The Turpentine Industry*, p. 337.

For Resins and Gums see ANDÉS, "Die Harzprodukte." Vienna, 1905.

ANDÉS.—"Gummi Arabicum." Vienna, 1896.

CORDENOY.—"Gommes, Résines." Paris, 1900.

„ "Plantes a Gommes et a Résines." Paris, 1911.

FRIEND.—"Introduction to the Chemistry of Paints." Longmans & Co., 1910.

LUTZ.—"Études chimique des Gommes." 1895.

TSCHIRCH.—"Die Harze und die Harzbehalter." Leipzig, 1906.

DIETERICH.—"Analysis of Resins, Balsams, and Gum Resins." London, 1901.

It is customary to use the term "gums" and "resins" synonymously, but this is a mistake. Strictly speaking, gums are those exudations of trees and plants generally that are either entirely or partially soluble in water, yielding sticky masses from which they are precipitated on the addition of alcohol. They are, therefore, used in the preparation of the so-called water varnishes, and are introduced into distempers on account of their binding properties. Resins, on the other hand, are insoluble in water, but usually dissolve in organic solvents such as alcohol, benzene, and turpentine. Clearly, therefore, it is incorrect to include benzoin and the dammars amongst the gums, and equally wrong to classify gum arabic and gum tragacanth as resins. It is not always easy to draw a sharp line of demarcation between gums and resins, but for all practical purposes it is well to bear the above distinction between gums and resins clearly in mind.

Broadly speaking, resins are brittle and lustrous. The Sierra Leone and Pebble copals are particularly good cases in point, being much prized by varnish manufacturers. Few of the varnish resins possess any distinctive odour, benzoin constituting the main exception, its pleasant aromatic perfume being familiar to all who have to deal with resins.

For the preparation of clear and colourless varnishes the palest resins are in great demand, and therefore fetch the highest prices. This is one of the reasons why cheap varnishes are darker and less transparent than those for which a higher price is paid.

We have already remarked that resins are soluble in organic solvents, but towards these reagents their reactions are both curious and interesting. Thus, for example, rosin and sandarac readily dissolve in alcohol, benzene, and turpentine, and are worked into varnishes with relative ease. Some of the other resins are insoluble in all the usual vehicles until after they have been fused by heat. This is true for the copals, and considerably enhances the difficulty and therefore the cost of manufacturing varnishes from them. As we shall see presently these peculiarities afford a very valuable means of identifying and distinguishing the resins.

**Statistics.**—The following figures show the value of the various gums and resins imported into the United Kingdom :—

	1906.	1910.	Value in 1910.
	Cwt.	Cwt.	
Gum arabic - - - - -	77,000	107,400	£176,000
„ kowrie - - - - -	128,000	157,000	638,000
„ lac-dye, seedlac, shellac, and sticklac	82,300	174,000	627,600
Other gums and resins - - - - -	213,500	223,200	559,000

The United Kingdom exported in 1910 about 27,000 cwt. of British-prepared gums (value, £68,000).

The United States *import* of industrial gums and resins is given by the following figures:—

	1906.	1910.	Value in 1910.
	Cwt.	Cwt.	
Gum arabic - - - - -	36,200	48,000	\$315,000
Chicle - - - - -	50,400	60,600	2,547,000
Copal, kauri, and dammar - - - - -	182,600	262,100	2,962,000
Gambier or terra japonica - - - - -	279,200	228,300	1,256,000
Shellac - - - - -	140,000	262,500	3,878,000
Tragacanth - - - - -	...	12,000	310,000
All other - - - - -	...	...	1,445,000

The export (principally to Canada) was in 1910: *Gum arabic*, 2,000 cwt. (value \$18,000); *chicle*, 15,000 cwt. (\$565,000); *copal and kauri*, 12,000 cwt. (\$165,000); *gambier*, 7,000 cwt. (\$41,000); *shellac*, 3,900 cwt. (\$84,000); all other, \$72,000.

For modern statistics see Appendix III.

## GUMS

**Gum Arabic** or **gum acacia** exudes from many plants, chiefly varieties of **acacias** growing throughout Australia, Asia, and Africa. As practically none of it comes from Arabia the term Arabic is unfortunate. The gum is essentially the calcium and potassium salts of arabic acid, and, by the addition of hydrochloric acid and alcohol to the aqueous solution of the gum, a fairly pure specimen of arabic acid may be obtained as a white amorphous mass to which the formula  $(C_6H_{10}O_5)_2H_2O$  is usually given.

Different specimens of the gum vary considerably in colour, the palest fetching the highest prices. Good qualities require only one and a half times their weight of water to effect their complete solution into a sticky mucilage of great value to stationers. Boiling with dilute sulphuric acid converts it into galactose.

When starch is gently warmed with dilute hydrochloric acid it yields a sticky fluid known as **British Gum** or **Dextrine** which is used as a substitute for gum arabic. It is usually prepared commercially by moistening starch with 2 per cent. nitric acid, and, after allowing it to dry in the air, heating the product to 150° C. (See p. 184 for manufacture.) When boiled with dilute sulphuric acid it yields *d*-glucose.

**Gum Tragacanth** is a different type of gum from the above, in that it is insoluble in cold water, and swells in hot water to a mucilaginous liquid that cannot be filtered. It is procured from several species of **astragalus**—a group of trees growing on the east of the Mediterranean.

**Chicle** is a Central American gum obtained from the white sap of gum-producing trees. It is first allowed to oxidise, then melted in a special rough oven of native manufacture, and the product so obtained is flavoured with brown sugar, coloured with stains, slightly flavoured with various flavouring materials, and then exported chiefly to America for use as a chewing gum.



**Tragasol.**—This gum is very similar in all respects to the pharmaceutical gum tragacanth. It is mostly used as a binding material, and in America tragasol is often sold as Tragacanth. Said to be used for carrying colour. American import in 1910 was 1,183,000 lbs. (value \$24,000).

**Gambier.**—Gambier is an extract obtained from leaves and small branches which grow on the islands in the East Indies. In commerce it occurs in brown earthy masses, and is imported chiefly from Singapore. It is used in medicine as an astringent, and is also employed by tanners and dyers.

## RESINS

The resins in common use are more numerous than the gums. We shall deal with them here in alphabetical order.

**Amber** is one of the most highly prized and valuable resins, having been used from the earliest times for ornamental purposes. Amber is found on the shores of the Baltic Sea, and it is also dug out of beds or mines in Germany, Poland, and certain parts of America. It is occasionally found on the Norfolk coast in this country, and has been picked up as far north as Sandsend and Whitby in Yorkshire. Its occurrence on our coasts is, however, too uncertain to render a British amber trade possible.

Amber is the resinous exudation of certain pine trees that existed ages ago, and are now probably extinct. At one time it must have been soft and viscous, for the remains of insects and vegetable matter are frequently found embedded in it. The largest piece of amber on record is that numbered amongst the royal jewels at Berlin in Germany, and weighs no less than 18 lbs.

As a varnish resin amber is very valuable, since it yields a varnish that offers a stout resistance to the action of the atmosphere. Unfortunately, however, its expense prevents its being used as much as would otherwise be the case.

It may be taken as an axiom that all good things are liable to unworthy imitation, and amber is no exception to the rule. It is not infrequently adulterated with common rosin or colophony, and, in order to increase the deception, insects and organic matter are introduced into the mass. Fortunately, however, adulteration of this kind is readily discovered in a variety of ways. For example, whilst amber melts at about 600°-615° F. (316°-324° C.), the adulterated product has a much lower melting point. It is useful to remember that two pieces of genuine amber may be readily joined together after softening the ends in a solution of caustic potash, whereas no such fusion occurs with the fictitious product, or at any rate, only with difficulty.

The name **Animi** is given to a pale resin found in Zanzibar. Like amber it is a fossil, being found embedded in the surface soil, covered with a reddish crust. When this is scraped off the characteristic "goose skin" appearance of the pure resin is laid bare. It is an excellent varnish resin, and is used in the manufacture of the best quality of coach varnishes.

A somewhat similar resin is collected by Arabs from certain trees direct, and goes by the name of "recent" or "virgin" animi. It is inferior to the true or fossil animi, and finds application in the manufacture of poorer qualities of varnish.

We have already had occasion to mention **Benzoin**, or "gum Benjamin," as it is frequently called, although, strictly speaking, it is not a gum. This resin is obtained from the *Styrax benzoin*, a tree growing in Sumatra and neighbouring islands. The tree is cultivated from seed, and in about seven years' time is ready for tapping. Each tree yields some 3 lbs. of crude resin annually, the product during the first few years being fragrant, soft, and pale. As the tree ages, however, the exudation becomes harder and too dark to be of service in varnish manufacture.

The properties of benzoin are subject to considerable variation according to the districts from which it is obtained. Thus, the Siamese product is brittle and



possessed of the strongest odour; whereas that from Sumatra is somewhat greyer in hue, less odoriferous, and possessed of a higher melting point.

Under the generic name **Copal** are included a large number of valuable varnish resins possessing a considerable variety of properties. Thus, some are soft, like the **Manilla copal**; others are hard and lustrous, the **Sierra Leone** and **Pebble copals** being cases in point; **Java copal** has a milky appearance; and so on. The bulk of the copals are obtained from Africa and America.

The various resins known as **Dammars** are found in India and the East Indies. **Batavian dammar** is used in the manufacture of coach and cabinet varnishes. Other varieties are known as **white, black, sal, and rock dammars** respectively.

An entirely different kind of resin from any hitherto mentioned is that known as **Dragon's Blood**, which is obtained from the dragon tree (*Calamus draco*) in Eastern Asia. To this end the fruit is allowed to ripen and the resin with which it is then covered is collected and cast into rolls approximately a foot long and an inch in diameter. As its name implies, it is possessed of a red hue, and is used in colouring or staining varnishes the same colour.

The term **Elemi** is generic like copal and dammar. The most important resin of this group, known as **Manilla elemi**, is obtained from the *Canarium commune*, a tree growing in the Philippine Islands. It finds application in the manufacture of varnish as a toughener.

**Gamboge** is obtained from the bruised leaves of a Siamese tree known as *Garcinia morella*. It is soluble in alcohol, and when taken as a medicine exerts a drastic purgative action upon the system. Like dragon's blood it is used for colouring varnishes, and water-colour artists employ it as a pigment.

**Gum Accroides** is the resinous secretion of certain Australian trees, and finds application in the manufacture of dark gold lacquers and yellow varnishes. The prefix "gum" is a misnomer.

One of the palest and most important of the New Zealand resins is known as **Kauri, Kowrie, or Cowrie**—a fossil occurring in the soil at various depths below the surface. It may also be obtained direct from living trees upon incision. In order to distinguish between the two varieties the latter is usually termed "young" kauri.

Of all the known resins, **Lac\*** is one of the most useful. It has been known for centuries, and the lac industry is one of great importance, so much so that in 1907-08 the total export from India was valued at £2,665,224. Lac differs from the resins hitherto described in that it is not the ordinary secretion of a tree or group of trees, but is produced by small insects known as *Tachardia lacca*, which feed upon the trees and excrete the lac. No fewer than eighty-seven different species of tree are known in India upon which the lac insect grows wild. When in the larval or caterpillar stage, colonies of these insects puncture the bark of the tree and suck up the sap, excreting a resinous mass which forms a light yellow encrustation round their bodies. After a few weeks the larvæ have developed into perfect insects, both male and female, the latter greatly preponderating in point of numbers. After impregnation the females become distended with a red liquid known as **lac dye**. The lac is now collected, the twigs upon which the colonies had collected being broken off by the natives and termed **stick lac**. This is crushed and washed, whereby the bits of wood are separated, and the product is known as **seed lac**. Further washing removes the dye, which is a marketable product, and the lac is melted and ladled on to a revolving cylinder whereby it solidifies in the form of thin flakes of **shellac**. Sometimes it is allowed to solidify in thicker discs and finds its way into the market as **button lac**. The terms **lemon lac, orange lac, and garnet lac** refer to the colour of the product, and this is determined to some extent upon the tree from which it has been obtained. **White shellac** or **bleached lac** is the ordinary shellac which has been bleached.

\* These remarks on lac have been culled from the interesting paper entitled "Technical Notes on Lac," read by A. F. Suter on 11th March 1909 before the Paint and Varnish Society.



Shellac is used largely in electrical work as an insulating material. It is also valuable for the preparation of knotting, varnish, etc.

**Mastic** is the exudation of the lentisc tree which flourishes by the Mediterranean. It is used in the preparation of picture varnish, and this, when mixed with linseed oil, constitutes megilp.

Hitherto we have used the word resin in a generic sense. Sometimes it is employed—but quite wrongly—to indicate the solid residue left behind in the stills after the extraction of the turpentine from the crude resinous exudation of the pine trees in France, America, and Russia. This product is really **rosin**, also known as colophony.

The best qualities of rosin are pale or amber coloured, and are used in making “finish” and the cheaper qualities of varnish. (See under **Turpentine Industry**.)

The last resin to be considered is **Gum Juniper** or **Sandarac**, which is obtained from certain North African trees. It is used in the manufacture of both spirit and oil varnishes, but in the latter case it must be first fused to render it soluble in the linseed oil.

For artificial resins see p. 211.

### Identification of Gums and Resins

From a chemical point of view, gums, and particularly the resins, are extremely complex, so that an analysis in the ordinary sense of the term is not possible. When heated the gums char and the resins readily burn with a luminous, smoky flame, showing the presence of a considerable quantity of carbon. If, therefore, we wish to identify the substances we shall have to judge usually by the cumulative evidence of a series of tests. These may be conducted as follows: \*—

1. **The Appearance.**—Dragon’s blood, gamboge, and the lacs may be distinguished by their colour. Mastic is usually in the form of small tears of a pale yellow hue, which soften when placed in the mouth. This enables us to distinguish it from sandarac, the only other resin with which it is likely to be confused. The “goose skin” surface of animi and the pebbles of pebble copal are distinctive, as is also the odour of benzoin. Gum acacia may be recognised by its taste and its resinous appearance, and gum tragacanth by its peculiar flakes.

2. **The Specific Gravity.**—This usually varies within narrow limits only. Care must be taken, however, to use only such specimens as are free from air bubbles, otherwise too low a value will be obtained (see table, p. 350).

3. **The Melting Point.**—The appearance of the gum or resin during the whole process of heating should be noted, as this is frequently characteristic. Many resins have no definite melting point (see table, p. 350).

4. **Behaviour towards various Solvents.**—This is most conveniently ascertained by shaking up a small portion of the resin with a little of the solvent in a tube, warming if necessary.

(a) **Water.**—Gum acacia and British gum dissolve in both hot and cold water. Gum tragacanth swells in hot water only, and rosin forms a semi-fluid mass. Elemi, dammar, shellac, and mastic become sticky in hot water, but amber, copal, and sandarac remain unchanged.

(b) **Caustic Soda.**—Amber softens and its ends can be fused together. Rosin partially dissolves. Shellac and the gums readily dissolve.

(c) **Ammonia.**—Rosin and gamboge dissolve at once. Copal, mastic, and sandarac soften and slowly dissolve. Amber, dammar, elemi, and shellac are unaffected.

(d) **Sulphuric Acid.**—The gums yield sugars on boiling with the dilute acid. All the resins dissolve in concentrated sulphuric acid, yielding a dark brown solution, save dammar and benzoin which usually afford a reddish hue.

(e) **Carbon Bisulphide.**—Dammar and rosin dissolve with ease. Elemi, mastic, and sandarac dissolve slowly. Copal usually softens, but amber and shellac do not dissolve.

(f) **Boiling Linseed Oil.**—Amber and copal are indifferent. Elemi, sandarac, and shellac dissolve slowly. Dammar, mastic, and rosin readily dissolve.

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\* It is here assumed, of course, that the gum or resin to be examined is one of those commonly occurring on the market and described in the preceding pages. It is usually exceedingly difficult and often impossible to identify with certainty the rarer specimens.

TABLE OF THE SPECIFIC GRAVITIES AND MELTING POINTS OF THE RESINS \*

Name of Resin.	Specific Gravity.	Melting Point, ° F.	Melting Point, ° C.
Amber - - - - -	0.98-1.20	600-615	316-324
Animi - - - - -	1.04-1.07	450-465	232-241
Asphaltum—lake - - - - -	1.38	189-210	87-99
„ land - - - - -	1.43	210-255	99-124
Benzoin—Borneo - - - - -	1.16-1.17	170-212	77-100
„ Penang - - - - -	1.14-1.16	170-212	77-100
„ Siam - - - - -	1.24	170-212	77-100
Copal—Angola - - - - -	1.06	...	...
„ Demerara - - - - -	1.03	450-465	232-241
„ Java - - - - -	1.03-1.04	347	175
„ Manilla - - - - -	1.06	230-250	110-121
„ Pebble - - - - -	1.055	...	...
„ Sierra Leone - - - - -	1.054	400	204
Dammar—Batavian - - - - -	1.06	260-300	127-149
„ Black - - - - -	1.09	...	...
„ Sal - - - - -	1.10-1.12	...	...
„ Singapore - - - - -	1.06-1.12	260-300	127-149
Dragon's blood - - - - -	1.20	248	120
Elemi - - - - -	1.02	170-250	77-121
Gamboge - - - - -	1.03	...	...
Gum accroides - - - - -	1.20	...	...
Kauri - - - - -	1.05	360-450	182-232
Lac - - - - -	1.10-1.20	...	...
Mastic - - - - -	1.06	221-248	105-120
Rosin - - - - -	1.04-1.10	117-212	47-100
Sandarac - - - - -	1.04	300	149

\* This table is compiled by kind permission of Messrs Longmans & Co. from Friend's "Introduction, etc.," p. 176.

(g) **Turpentine.**—Amber, shellac, and the gums are insoluble. Benzoin partially dissolves. Elemi, mastic, rosin, and sandarac dissolve easily.

(h) **Alcohol.**—Amber and the gums are insoluble. Dammar may partly dissolve, and copal becomes softened. Elemi dissolves with difficulty. Benzoin, gamboge, mastic, rosin, sandarac, and shellac readily dissolve.

(i) **Benzene.**—Amber, copal, shellac, and the gums are indifferent. Elemi and sandarac dissolve, but less readily than dammar, mastic, and rosin.

In applying these tests, however, it must be borne in mind that different samples of the same gums and resins are liable to show irregularities and slight variations in their properties, so that due care must be taken before conclusions are drawn.

See also under **The Plastic Industry.**



SECTION IX



The Rubber Industry





# THE RUBBER INDUSTRY

## I.—NATURAL RUBBER, GUTTA-PERCHA, AND BALATA

BY A. J. CARRIER, B.Sc. REVISED BY D. E. PARTINGTON, A.I.R.I.

### LITERATURE

MEMMLER.—“Science of Rubber.” London, 1934.

DAVIS AND BLAKE.—“Chemistry and Technology of Rubber.” London, 1937.

“Rubber Industry in Germany during the Period 1939–1945.” B.I.O.S. overall report No. 7. H.M. Stationery Office.

### INDIARUBBER

**General.**—Indiarubber is nearly always obtained, in the first instance, as a milk (latex) which exists in the form of a negative emulsion (*i.e.*, the drops of rubber carry a negative charge) between the outer bark and the cambium, and which is coagulated and, if obtained from a plantation, washed and dried. This product is exported, and is subjected by the rubber manufacturer to a series of processes comprising further washing and drying, the “crepe” obtained being rendered plastic by heating and kneading (mastication) prior to adding vulcanising and other ingredients, where necessary. The mixture is now moulded by rolling, if for sheets, or into other forms, and is vulcanised. This is the process usually employed for “mechanical” goods.

### Sources of Rubber

(a) **Euphorbiaceæ**—(1) *Hevea*. About 60 per cent. of the total output of rubber is obtained from the *Hevea brasiliensis* of Para, Amazonas, and Brazil, which is the tree almost always grown on the Eastern plantations. It grows to a height of 100 ft., with a diameter up to 40 ins. (2) *Manihot* (Brazil). The native allows the latex to coagulate naturally as it flows down the tree—it yields Maniçoba or Ceara scraps. (3) *Sapium* (Colombia) yields Colombia, Virgin, and Carthagena scraps. (4) *Urcandras* (Upper Amazon), mixed with Negro-heads, etc., from Para.

(b) **Apocynaceæ**—(1) *Funtumia* (tropical Africa), gives a rubber of high quality, known as Gold Coast Lumps, Ivory Coast Lumps, Niger Niggers, etc. (2) *Landolphia*, or Vine Rubbers (Congo, etc.). Best known brands are Red and Black Kassai, Upper Congo balls, Equateur, Madagascars (such as Virgin sheets, Pinky), and Sierra Leone Niggers. (3) *Clitandra* (Gold Coast and Congo). (4) *Hancornia* (Brazil), yields Mangobeira. (5) *Dyera* yields Jelutong, of which Palembang and Pontianac, or Dead Borneo, are the best known brands.

(c) **Urticaceæ**—(1) *Ficus*, of which *Ficus elastica* or Rambong (Burmah, Ceylon, Malaya, Java, India, etc.), is the best known, and which yields brands known as Assam, Rangoon, Java, and Penang. (2) *Castilloa* (Mexico, Central America, etc.), yields Peruvian “Cancho,” Cancho Negro, Mexican Strips, Centrals.

(d) **Compositæ**.—*Parthenium Argentatum* Gray, a shrub, yields Guayule.



FIG. 155.—Para Rubber Tree Thirty Years Old, showing Full Herring-Bone Tapping, Botanic Gardens, Singapore. (By kind permission of the Malay States Development Agency, London.)



From the latex of any of these species it is possible to prepare a dry rubber containing from 1.5 to 3 per cent. of resin for *Hevea*, *Castilloa*, and *Manihot*, and 5 to 7 per cent. for *Ficus*, *Funtumia*, and the better *Landolphias*, and not more than 3 to 5 per cent. jointly of ash, proteid, and other substances. However, many raw rubbers as imported contain admixed earth, bark, stones, etc.

One system of "tapping" or obtaining latex, in use on Para plantations, is illustrated in Fig. 155, and consists in paring away, daily or on alternate days, a narrow strip of bark along the lower sides of a series of slanting cuts leading into a central cut, at the bottom of which a cup for receiving the latex is placed. When the bark has been removed over a sufficiently wide area, the tree is allowed a rest for some three or four years. The most general system of tapping is the "half herring-bone." The *Hevea* tree gives, per annum, some 2 to 3 lbs. of rubber for 150 to 160 tapplings, the *Castilloa*, 1 lb. for 4 to 5 tapplings.

*Hevea* trees should be over five years old before they are worked for rubber. In the case of smaller rubber shrubs, such as guayule, where tapping is inapplicable, the rubber is obtained by extracting with solvents or by mechanical processes in which the shrubs or the rich bark are pulped, and the pulp run into settling tanks; the rubber and a portion of the bark float on the surface. Guignet's process, which depends upon mechanical attrition and agglomeration of the rubber by friction, is described in British Patent Specifications, Nos. 18,375, 1910, and 9,064, 1909.\*

*Nature of Latex.*—Latex consists of a fluid in which globular-shaped particles are suspended. These particles show typical "Brownian" movement, and wander to the anode if an electric current be passed through the latex, which may, therefore, be looked upon as a negative colloidal emulsion. This Brownian movement may be modified or caused to cease entirely by the addition of certain reagents, dilution, boiling, or by the electric current. Rubber latices contain, in addition to rubber, water, resins, proteid, mineral matter, peptones, sugars, simple albane-like oxygen derivatives, and various enzymes, such as oxydase, peroxydase, and catalase.

The following analyses give the composition of latex:—

	Seligmann.	Scott.	Bamber.
	Per Cent.	Per Cent.	Per Cent.
Water - . . . . .	55.56	52.32	55.15
Rubber - . . . . .	32	37.43	41.29
Protein and albumen - . . . . .	2.3	2.71	2.18
Resin - . . . . .	traces	3.44	...
Ash (mineral substances) - . . . . .	...	0.23	0.41
Sugar - . . . . .	...	4.17	0.36
Oil - . . . . .	9.7	traces	...

**Coagulation.**—1. The old process of coagulating by smoking on "paddles," still carried on in the Amazon district in the production of "fine Para," is as follows: A fire producing dense smoke is made from *Urucuri* nuts, palm leaves, etc.; the paddle, after being coated with latex, is supported on a bar over, but not too near, the fire, and is rotated by hand until coagulation occurs. This process is repeated to build up a succession of films forming a ball of the desired size.

2. Coagulation is also effected by means of acetic acid (practically the only method employed on plantations), sulphuric and hydrofluoric acids, alcohol, etc., or simply by exposure to air.

3. Centrifugal machines have also been successfully used, the minute drops of rubber suspended in the latex being forced together as a soft mass on the circumference of the rotating drum by centrifugal force, the clear rubber-free liquid being left in the centre.†

4. A continuous electrolytic method and apparatus has been proposed, dependent upon the "Brownian" movement, for separating caoutchouc from

\* See also Patent Specifications, No. 23,682, 1912.

† See Patent Specifications, Nos. 330, A.D. 1905, and 7,433, A.D. 1909.





FIG. 156.—Plantation Washing Machines.

latex.\* The fine drops of rubber which carry negative charges collect on an endless moving anode, upon which the latter is poured, and from which the coagulated rubber is continuously removed.

5. A method known as the Hopkinson spraying method admits the latex to the top of a tower of hot air in the form of a spray. As the droplets of latex pass down the tower the water evaporates and dry rubber in powder form collects at the bottom. This produces a "whole latex rubber," *i.e.*, only the water is removed and all the serum substances remain in the rubber. This is a very tough and fast-curing rubber.

6. The latest method, suggested by the British Rubber Producers' Research Association (B.P. 593,688), is to coat an endless belt with coagulant, pass it through the latex, thus receiving a film of coagulum which is stripped and passes into a spray washing chamber and then into a drying chamber. Dry rubber is reeled up at the exit end of the machine.

**Funtumia** and some other latices may be coagulated merely by heating to 100° C.

**Castilloa** is best coagulated by "creaming," a process in which water is added and a cream collects upon the surface.

**Negro-heads** result by pressing together the scraps of prematurely coagulated rubber found on the tree, or in the collecting or coagulating vessels.

Premature coagulating during transport from the trees to the factory is usually prevented by addition of water, and occasionally formalin, ammonia, etc.

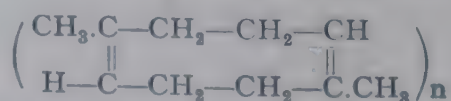
**Washing and Drying.**—(1) *On the Plantation.* Chemically coagulated plantation rubber, after being removed from the watery liquid upon which it is found floating, is passed through washing rolls somewhat similar to those shown in Fig. 158 (see p. 358) in order to remove mother liquor, etc.

It is advisable to employ a battery of three washing machines, No. 1, with rolls running at differential speeds, set wide and with water spraying on them; No. 2, differential and set close with water spray; and No. 3, equal speeds, plain and set close, with no spray. The resulting sheets are about  $\frac{1}{8}$  in. thick, and are dried in well-ventilated corrugated iron sheds with racks over which the sheets are hung. This method produces "pale crêpe," which is a pale straw coloured or colourless rubber used for light coloured articles.

If "smoked sheet" is to be made the lumps of coagulum are first passed through plain rolls with even speeds and water spray where they receive a gentle squeeze. This removes only part of the serum substances. Then the sheets are put through even speed rolls bearing a ribbed profile and no spray. This produces sheets  $\frac{1}{8}$  in. in thickness with a ribbed pattern to prevent adhesion when packed. They are then hung up in a shed on racks, and smoke is blown in to dry and preserve them. When dry they are brown in colour and have a strong "smoky" odour.

**Constitution and Properties of Caoutchouc.**—Caoutchouc consists of a highly polymerised hydrocarbon of formula  $[C_{10}H_{16}]_n$ , mixed with some resin, proteid, mineral matter, etc.

According to *Harries* † it contains an eight carbon ring chain, thus:—

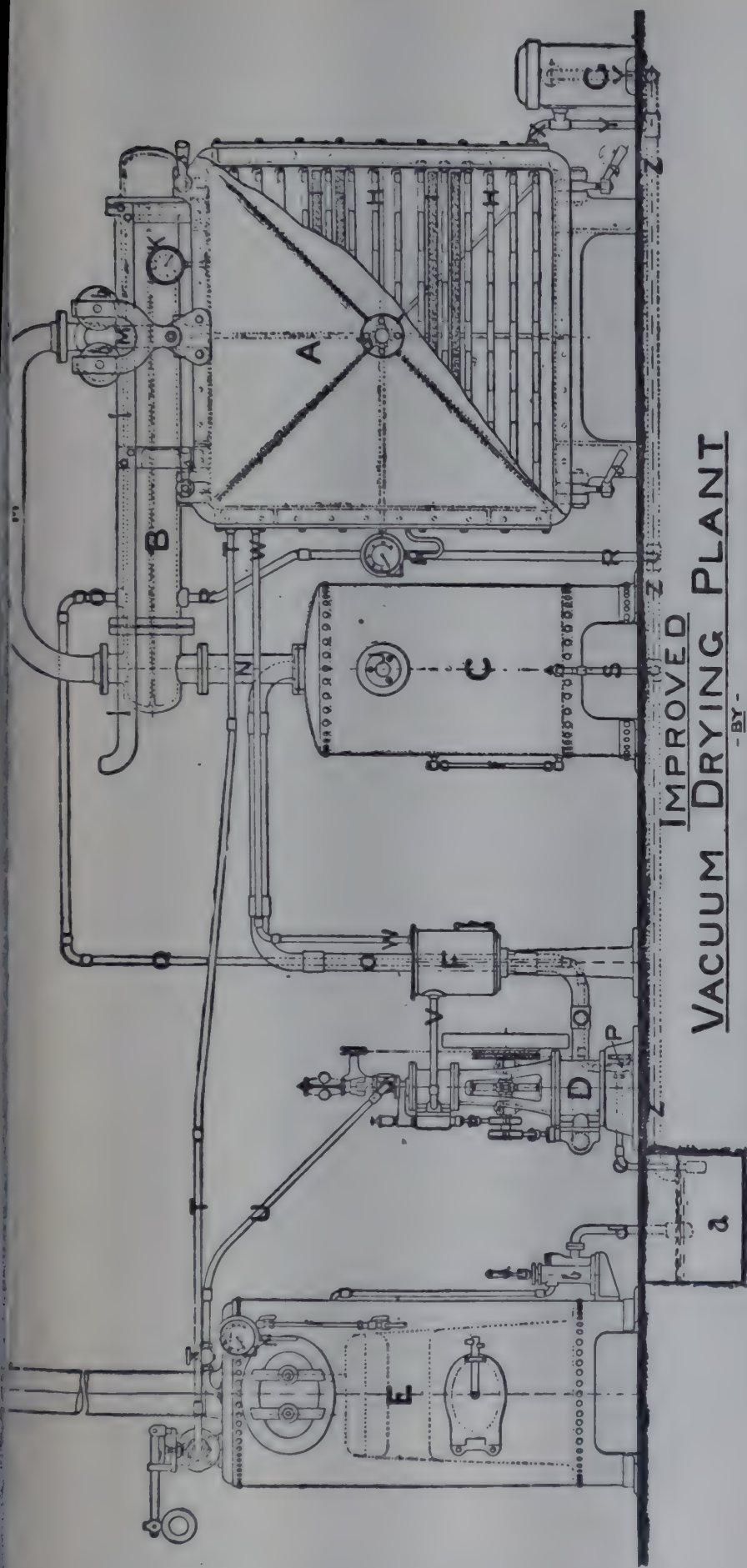


He bases this conclusion on the fact that he succeeded in combining the rubber molecule with

\* See Patent Specifications, Nos. 21,441, A.D. 1908, and 5,854, A.D. 1910.

† See *Harries*, "Ber.," 37 (1904), 2,708; 38 (1905), 1,195, 1,198, 3,985, 3,989.





## IMPROVED VACUUM DRYING PLANT

-BY-

DAVID BRIDGE & CO ENGINEERS CASTLETON MANCHESTER

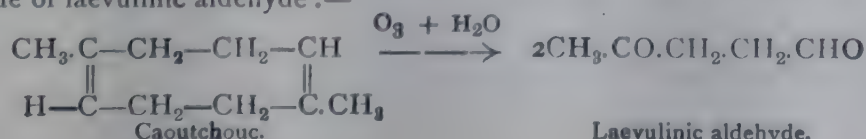
A. Vacuum Chamber or Stove  
B. Surface Condenser  
C. Receiver  
D. Steam-driven Air Pump  
E. Oil Separator made under Baker's Patent  
F. Steam Trap  
G. Steam-heated Grid Coils  
H. Galvanised Iron Wire Trays  
I. Sight Glasses  
J. Vacuum Gauge

L. Steam Gauge  
M. Air Pipe from Stove to Condenser  
N. Air Pipe from Condenser to Receiver  
O. Air Pipe from Receiver to Air Pump  
P. Water Circulating Pump  
Q. Water Pipe to Condenser  
R. Water Pipe from Condenser to Drain  
S. Water Pipe from Receiver to Drain

T. Steam Pipe to Heating Grids in Stove  
U. Steam Pipe to Engine  
V. Exhaust Steam Pipe from Engine to Oil Separator  
W. Exhaust Steam Pipe from Separator to Heating Grids in Stove  
X. Exhaust Steam Pipe from Heating Grids to Steam Trap  
Y. Exhaust Steam Pipe from Steam Trap to Drain

Z. Drain to Tank in Floor  
a. Water Tank in Floor  
b. Hand Boiler Feed Pump  
d. Suction Pipe. Tank to Pump  
e. Suction Pipe. Tank to Circulating Pump  
f. Water Gauge Glasses  
h. Runners Carrying Door of Stove  
l. Rail for Runners  
s. Swing Bolts for Door of Stove.

ozone, thus producing the ozonide  $C_{10}H_{16}(O_3)_3$ , which with water split up into laevulinic aldehyde and a superoxide of laevulinic aldehyde:—



Laevulinic aldehyde.

NOTE.—The Stove Door partly broken away to show Interior.

FIG. 157.

Rubber when hydrolysed yields ozonides, laevulinic acid, and laevulinic aldehyde. A current of air passed through a warm benzine solution yields  $C_{10}H_{16}O$  and  $C_{10}H_{16}O_3$ . Cl and I acting on a  $CHCl_3$  solution yield  $C_{10}H_{14}Cl_8$  and  $C_{10}H_{16}I_2$  respectively, but it is doubtful whether these are definite compounds. Bromine derivatives are  $C_{10}H_{16}Br_4$ ,  $C_{10}H_{15}Br_5$ . Various nitrosite and nitrosate compounds

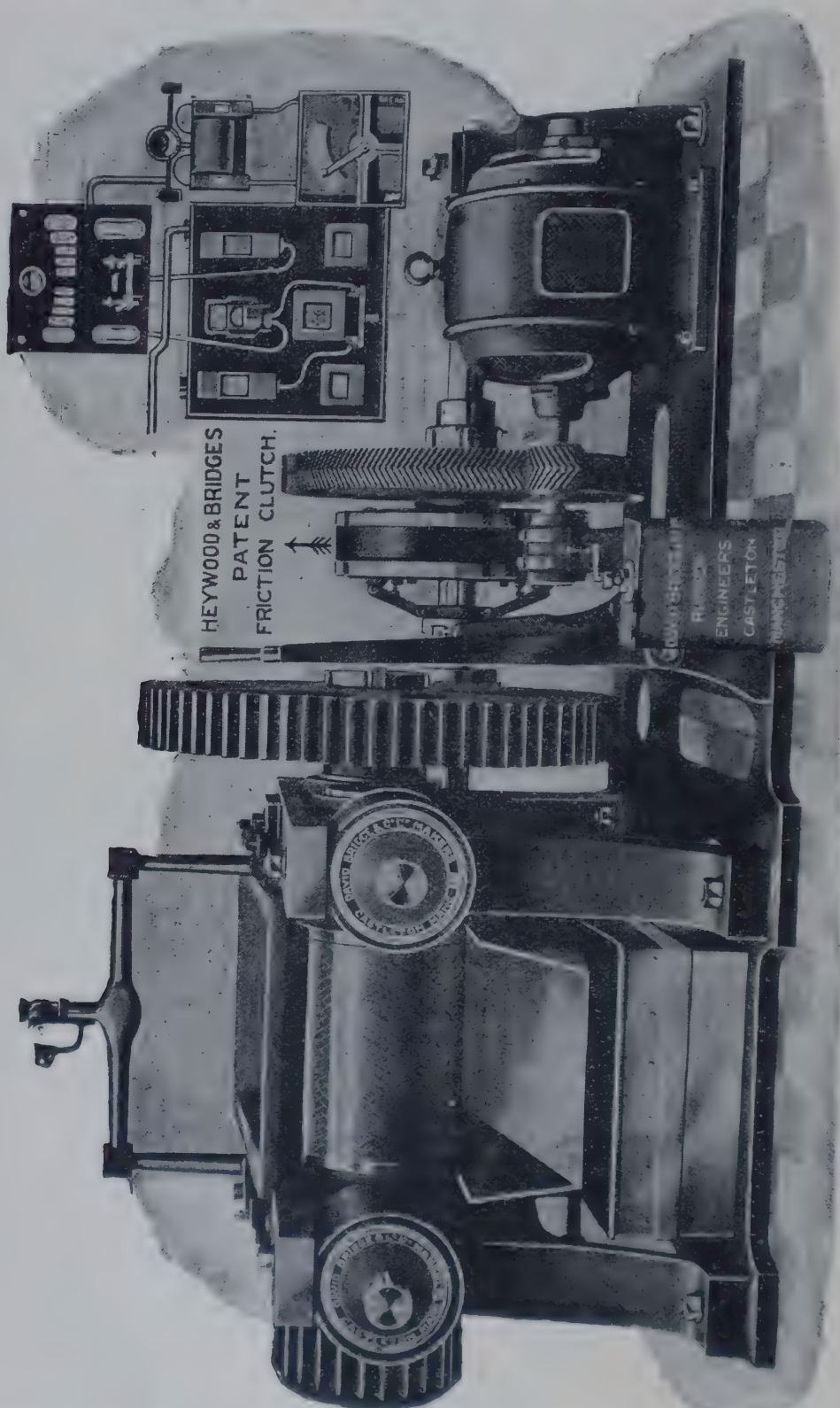


FIG. 158—Washing Mill.

have been prepared; for example, with nitrous acid caoutchouc in benzine solution forms a yellow nitrosite,  $C_{10}H_{15}N_3O_7$ . When distilled, caoutchouc yields a mixture of **isoprene** ( $C_5H_8$  or  $CH_2=C(CH_3)-CH=CH_2$ ), B.P.  $37^\circ C.$ , and dipentene,  $C_{10}H_{16}$ , B.P.  $171^\circ C.$  And conversely caoutchouc may be artificially produced by the polymerisation of **isoprene**, which has been industrially produced on the large scale for the manufacture of synthetic rubber.

According to Harries, caoutchouc is produced by the condensation of pentose sugars contained in the plant, just as starch and cellulose are produced from the condensation of hexose sugars. In



other words, rubber is a multiple of the hemiterpene group,  $C_5H_8$ , just as cellulose and starch are multiples of the hexose groups,  $C_6H_{10}O_5$ . Harries showed that Para rubber exists in three forms, an oily, the ordinary soluble form, and an insoluble modification.

Under ordinary pressures fine Para melts about  $188^\circ C.$  to a gummy mass, simultaneously undergoing decomposition as does vulcanised rubber when melted. Under high pressure, however, and in the absence of air, vulcanised rubber may be melted to a fluid mass and heated to higher temperatures than  $400^\circ F.$  without decomposition or loss of elasticity on cooling. Advantage is taken of this fact in the regeneration of rubber (see later). Unvulcanised caoutchouc is characterised first by its extraordinary elasticity at  $15^\circ$ - $20^\circ C.$ , and secondly, by its plasticity at  $50^\circ C.$ , so that when warmed it can be pressed into any shape and intimately mixed by kneading with other substances. At  $0^\circ C.$  it becomes hard. Freshly-cut surfaces of unvulcanised rubber may be made to adhere to one another at ordinary temperatures without using a solvent. The specific gravity of latex is about 0.976; of freshly coagulated rubber, which shows a reticulated structure, about 0.91-0.926. Raw rubber absorbs water and increases in volume.

"**Tackiness**" in raw rubber is an abnormal condition. The following causes have been observed or suggested: Sunlight, heat, bacteria, enzymes, faulty coagulation, small quantities of specific chemical substances, absence of moisture, and the presence of excessive moisture.

Vulcanised as compared with raw rubber is stronger, more resilient, more elastic, more stable towards actinic rays, solvents, and reagents, less changeable under variations of temperature, *e.g.*, it does not harden on moderate cooling, or soften under moderate heating, and is not adhesive. It is only slightly attacked by alkalies or dilute acids, unless, of course, it contains fillers which are acted upon by these reagents; conc.  $H_2SO_4$ , or  $HNO_3$ , and oils readily attack it.

The perishing\* of rubber, which is hastened by exposure to strong light and warmth (say  $50^\circ$ - $70^\circ C.$ ), is usually due to oxidation, which results in the formation of resinous compounds and traces of sulphuric acid; and to faulty curing resulting in "after-vulcanisation" if an excess of free sulphur be present. It has been shown that soft rubber changes but slightly if kept in the dark at ordinary temperatures, whether wet or dry. The effect of light on rubber is of great importance in connection with balloon fabrics. V. Henri, as the result of recent experiments, came to the conclusions that crude rubber should not be used in balloon work, and that the cloth employed and the rubber should be coloured with an ultra-violet screen, such as chrome yellow. A high grade soft rubber breaks at about ten times its original length, and the load at breaking will be about 10 tons to the square inch, *i.e.*, since rubber is practically incompressible, 1 ton to the square inch of the original section. A well-made rubber buffer may be compressed many thousand times to about one-third its original thickness without lasting effect.

The extension curve of a good rubber shows a reversal of sign, usually at double the original length, accompanied by a flattening of the curve.

**Solvents for Rubber.**—Unvulcanised rubber swells up, however, when mixed with solvent naphtha, benzol, benzine, carbon bisulphide, carbon tetrachloride, chloroform, petroleum-ether, benzaldehyde, camphene, oil of turpentine, caoutchoucine (dipentene), etc., and forms what may be termed "colloidal solutions," as distinguished from true solution—the rubber having a sponge or foam-like structure, and the solvent, diffusing in by osmose between the walls, distends the rubber network into what we call a "solution." A solution is more easily obtained by treating the rubber immediately after mastication.

Spence and Kratz (*Kolloid Zeitschrift*, xiv., p. 262, 1914) found that the addition of small quantities of some acids greatly facilitates the solution of raw rubber, thus with the addition of 0.3-0.5 g. of  $CCl_3COOH$ , 100 g. of dry washed rubber could be dissolved in 1,000 c.c. of  $C_6H_6$  in the cold in forty-eight hours.

Patents cover the production of non-inflammable solutions by using carbon tetrachloride, dichlor-methane, tri- and tetra-chlor ethane or tri-chlor benzol. Acetone and alcohol do not dissolve rubber.

**Hot Vulcanisation.**—Without vulcanisation it is doubtful whether there would be a rubber industry worthy of the name. The hot process, discovered by Goodyear in 1839, depends essentially upon mixing raw rubber, as described later, with 0.5-3 per cent. of sulphur, 0.1-2 per cent. of an accelerator, 2 per cent. of

\* W. O. Ostwald and Walter Ostwald (Patent Specification, 10,361, 1910) claim a process for regulating the changes produced by auto-oxidation and polymerisation in rubber, etc., by treating it with neutral and basic aromatic nitrogen compounds, or neutral and basic heterocyclic substances or alkaloids (see p. 361, "Accelerators").



metallic oxide (usually zinc oxide), and in some cases 1 per cent. of fatty acid. This mixture is then heated at temperatures from  $100^{\circ}\text{C}$ . to  $150^{\circ}\text{C}$ . for a few minutes up to one hour, depending upon the particular accelerator used and its amount.

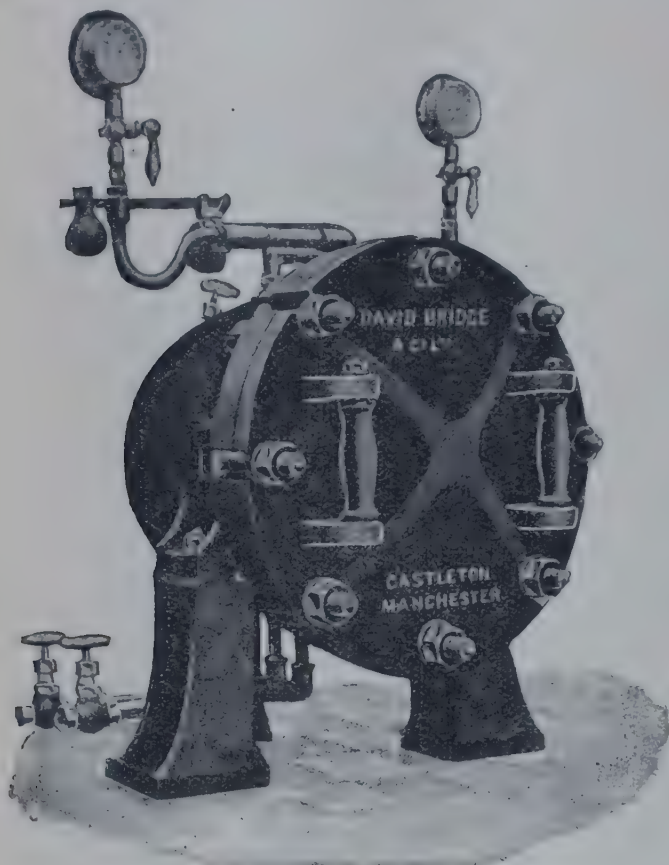


FIG. 159.—Vulcaniser Closed.

speed through a steam-jacketed or otherwise heated chamber. The hot air process is applicable to other classes of goods, but is seldom used with proofed cloth.

**Vulcanite, Ebonite, and Hard Rubber** are produced by employing a considerable excess of sulphur, say 40 per cent., and by extending the vulcanising

Hot vulcanisation yields best results when the goods are under high pressure, which is obtained either in presses or by wrapping tightly with fabric, *e.g.*, for curing hose and tyres. In the *open* or *steam cure* live steam is admitted into a kind of autoclave (Figs. 159 and 160), into which the goods, wrapped with canvas or in moulds, are placed; the vulcanising chamber is sometimes steam-jacketed. *Press-curing* is carried on between the steam-heated platens of hydraulic presses. This process has the advantage of high pressure. In recent years the presses have been fitted with chambers into which the lower platens are raised, thus combining the advantages of the live steam and press cures. *Continuous processes*.—In order to enable great lengths of cable, hose, and proofed fabrics to be cured uniformly, they are passed at a regulatible

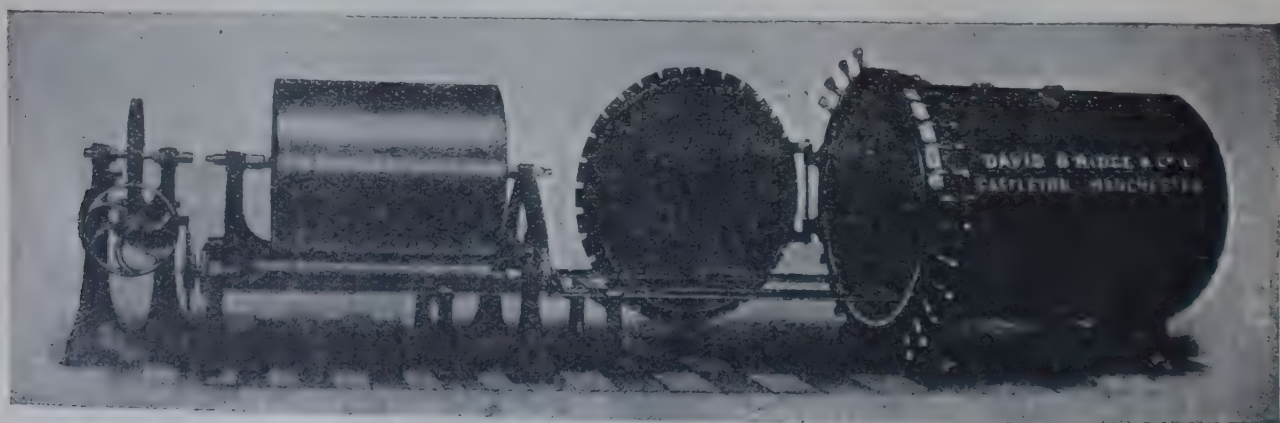


FIG. 160.—Vulcaniser Open. (David Bridge, Manchester.)

operation over 6 hours. Such hard sorts of rubber are used for making combs, handles, etc., and in the electrical industry as an insulating material. It should be unacted upon by acids and alkalis.

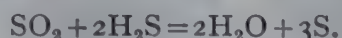
**Cold Vulcanisation**, discovered by Alexander Parkes in 1846, and applied more particularly to the vulcanisation of proofed cloth, is brought about by means



of a 2–3 per cent. solution of sulphur chloride in  $\text{CS}_2$ . This process is not applicable to thick goods. The rubber mixing, which is conducted in the usual manner, as described later, but without the addition of sulphur, is rolled out into a sheet and dissolved in naphtha. The swollen dough, rendered homogeneous by being worked between rolls, is spread upon the cloth in the machine shown in Fig. 162. The fabric is placed on a roller, as shown at the right hand of the figure, then it is passed over the upper roller, above which is situated a doctor for adjusting the thickness of the layer, and in front of the doctor the dough. In its passage over the steam-heated table B, the fabric is freed from solvent. As a general rule a number of layers are applied. The fabric is now conveyed to another machine, upon which it is cured by unwinding it from one roller and winding it upon another, by allowing it in its passage to contact with a third roller dipping into the sulphur chloride bath.

Alternatively, the proofed cloth is festooned in a large room and sulphur chloride vapour blown in.

**Peachey Process of Cold Vulcanisation** (see English Patent 129,826, 1918).—The process consists of treating rubber with sulphur dioxide gas and hydrogen sulphide gas. These two react, producing nascent sulphur, thus:



The nascent sulphur then unites with the rubber at ordinary atmospheric temperature, thus bringing about effective vulcanisation.

Rubber sheet, either dry or wetted with benzene, may be submitted successively, and, if necessary, repeatedly, to atmospheres containing sulphur dioxide and hydrogen sulphide respectively; or the gases may be applied successively to ordinary rubber solution. In the latter case the solution rapidly becomes more viscous, and ultimately forms a jelly, which is no longer soluble in the solvent.

In English Patent 136,716, 1919, Peachey suggests accelerating the action by adding 0.5 per cent. of nitrosobenzene or other nitroso compound. As this process is a cold one and does not involve the use of sulphur chloride, it renders possible the use of a large variety of organic filling and colouring agents, most of which are unaffected by exposure to sulphur dioxide and hydrogen sulphide.

By means of this process rubber can be used as a binding agent for materials such as cork dust and wood meal, the mixings being sheeted and vulcanised, forming a cheap and excellent floor covering. Leather waste can similarly be converted into reformed leather suitable for use in the manufacture of boots, shoes, and upholstery. Shoddy waste yields a felt-like material. It can be applied to dissolved rubber, and gives good results for repair work.

**Accelerators.**—Some substances when introduced into rubber mixings considerably shorten the time required for vulcanisation, hence they are called accelerators.

The more important inorganic compounds are  $\text{PbO}$ ,  $\text{CaO}$ ,  $\text{MgO}$ , and  $\text{Sb}_2\text{S}_5$ , and soft resinous rubbers, which cannot be properly vulcanised when mixed with S alone, can be cured with the aid of these accelerators.

Esch and Seidl have shown that  $\text{PbO}$  stimulates the reaction between the S and the rubber resin, which is accompanied by the evolution of much heat.

Inorganic accelerators are now seldom, if ever, used, having been replaced by organic accelerators, without which the rubber industry as it exists to-day would not be possible.

They are all much more powerful than inorganic compounds, and some are so extremely powerful that it is possible to vulcanise rubber with some of them at room temperature overnight. Examples in order of speed are as follows:—

“Butyl Eight” (a proprietary accelerator sold by the Anchor Chemical Co.).

Zinc diethyl dithiocarbamate.

Zinc isopropyl xanthate.

Tetramethylene thiuram disulphide.

Mercaptobenzthiazole.

Diphenyl guanidine.

The average cure with modern accelerators in the manufacture of mass produced press cured articles is a few minutes at 50 lbs./in.<sup>2</sup> steam pressure.

Tetramethylene thiuram disulphide will vulcanise without sulphur if used in amounts above  $\frac{3}{4}$  per cent. This is used to produce super ageing compounds, since the presence of free sulphur is largely responsible for the deterioration of rubber after cure.



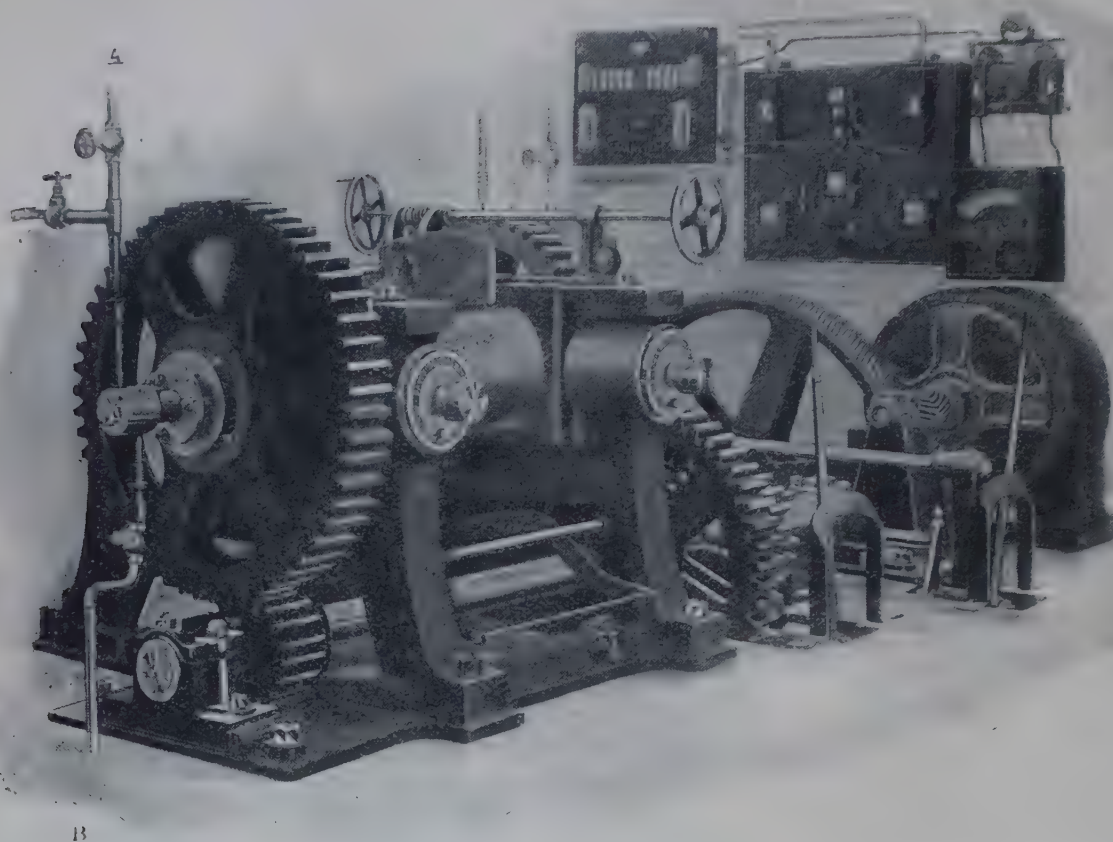


FIG. 161.—Grinder and Mixer. (David Bridge & Co., Castleton, Manchester.)

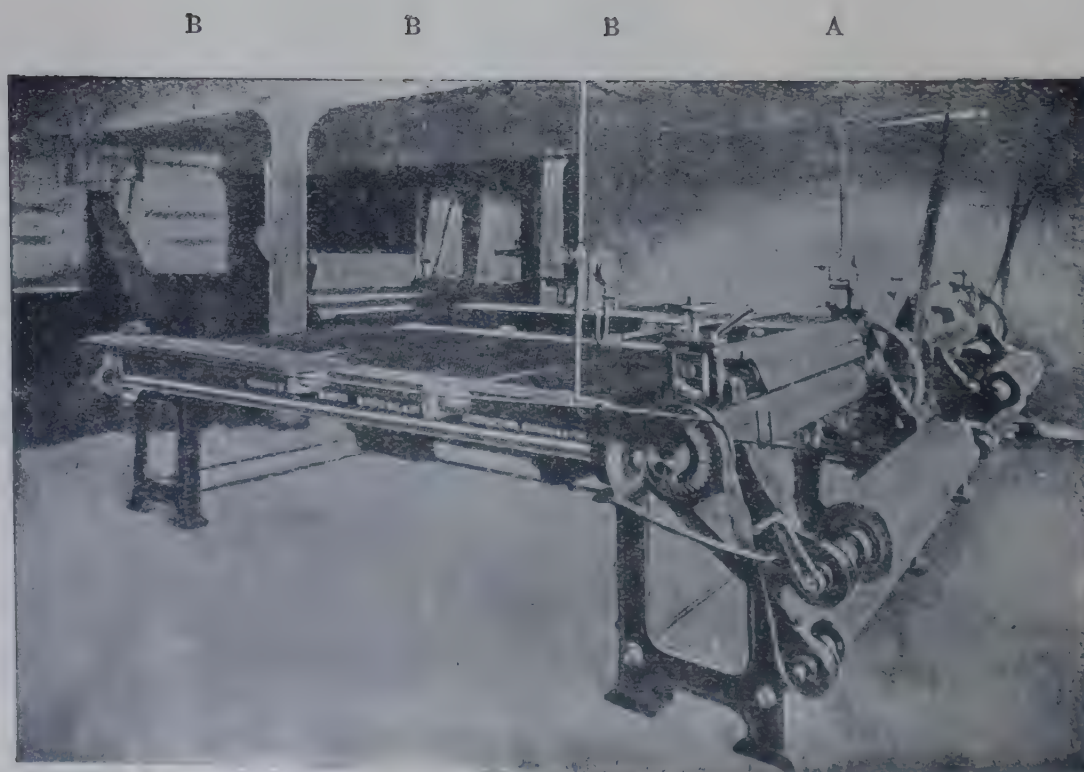


FIG. 162.—Spreading Machine (for garment cloth, card clothing, fine sheet, waterproofing, etc.).



In addition to the above advantages, organic accelerators impart greatly improved ageing because of the smaller amounts of sulphur which their use permits, and greatly improved tensile strength due to the lesser heat degradation of shorter cures.

The range of such accelerators is very versatile. There is one for almost any purpose. For example, some are only active at fairly high temperatures, *e.g.*, Benzothiazole disulphide, so that there is no fear of vulcanisation taking place prematurely during processing, but when the temperature is raised in the cure the full effect of the accelerator can be utilised.

There are some which are composed of organic compounds, not necessarily accelerators, which react to produce an accelerator during cure. These are known as delayed action accelerators. They are very useful where complicated mouldings are being made which require time for the rubber to flow before cure sets in.

**Theory of Vulcanisation.—Hot.**—Weber concluded from his experiments that direct addition results in the formation of compounds varying from  $(C_{10}H_{16})_{10}S_2$  to  $C_{10}H_{16}S_2$ , but this is very doubtful. *Erdmann* (*Liebig's Annalen*, 1908, 362, p. 133) assumes the formation of thiozonides corresponding with the ozonides. *Hübener* (*J.S.C.I.*, 1910, p. 289) concludes that mono- and disulphides are formed. *Bysow* assumes that in the primary stage mere physical absorption occurs.

*Kirchhof* (*Kolloid Z.* 13, 49 (1913), 14, 35 (1914)), believes that rubber only reacts with a certain active form of sulphur, and *Bedford and Sebrell* ("Chemistry and Technology of Rubber," *Davis and Blake*, p. 246) succeeded in separating a form of sulphur from sulphur dioxide and hydrogen sulphide in benzene, which would vulcanise at room temperature.

The amount of combined sulphur bears no relationship to the state of cure.

*Boggs and Blake* (*Ind. Eng. Chem.*, xxii., 744, 748 (1930), xxvi., 1283 (1934)) believe that sulphur reacts in more than one way. If it reacts with the unsaturated terminal groups of the rubber molecule, soft rubber is formed. If it reacts with the double bonds, hard ebonite is formed.

**Cold.**—The earlier experiments of *Henriques and Weber* led them to assume the formation of direct addition products, according to *Weber* varying from  $(C_{10}H_{16})_{24}S_2Cl_2$  to  $(C_{10}H_{16}S_2Cl_2)_{24}$ . *Hinrichsen* assumes the formation of a body,  $(C_{10}H_{16})_2S_2Cl_2$ , which forms a solid solution with the rubber, this solid solution containing varying quantities of absorbent "free sulphur." *W. O. Ostwald* has recently propounded a theory of both hot and cold vulcanisation to the effect that colloidal absorption occurs and not chemical reaction, but this seems to be disproved by the experiments of *Alexander*, who has shown that the tetrabromide and nitrosite derivatives obtained by precipitation from solutions of vulcanised rubber contain all the S of vulcanisation.

**Manufacture of Rubber Goods.—Mixing**—For certain classes of goods, such as cut sheet and elastic thread, sulphur is the only ingredient added, but in general other additions are made, sometimes to the extent of 75 per cent., *viz.*, *fillers*, such as factis, or "oil substitute" (see under rubber substitutes), chalk, talc, rubber waste, etc.; *pigments*, such as "golden" sulphide (antimony sulphide), lithophone, cinnabar, etc.; *for toughening*, balata, magnesia, zinc oxide, kaolin, carbon black, etc.; *for closing pores*, bituminous substances, etc.; *for assisting processing*, oils, waxes, plasticisers. The mixing machine (Fig. 161), resembles the washer already described. The rolls are smooth and hollow for receiving steam or cold water supplied to trunnions through pipes, A, B, and are run at differential speeds. The raw rubber sheet is rendered plastic at about 50° C. by being passed a number of times (*masticating*) through the heated rolls of the mixer, gradually closing the "nip."

First the softeners, such as oils or bitumen, are added, then the accelerator followed by the fillers, etc. The sulphur is added last. After each addition, much falls through into the tray beneath the rolls. This is swept up repeatedly until it is all absorbed by the rubber.

**Calendering.**—When a homogeneous sheet has been obtained it is usually taken direct to the calendar (Fig. 163), the bowls of which must be truly turned, are very heavy and are also steam-heated. For the production of ordinary sheet (1 mm.—1 cm. thick) the bowls run at even speed, and the dough is placed in the nip of the two upper bowls. The rotation of the bowls carries it round as a thin sheet to the lower nip, where it is transferred to a cloth which passes between the lower bowls and is wound upon a roller shown in front of Fig. 163, the cloth preventing adjacent layers from cohering. After an interval of rest the sheet is vulcanised. The process of building articles from calendered sheets is termed "*making up*," and requires great skill.



The calender can also be used for proofing fabric. For this, the rubber is made to adhere to the middle roll and the fabric is passed through the middle and lower bowls set so that it is just nipped. These two bowls run at friction speeds. By this means the rubber is forced into the meshes of the cloth, leaving the bowl clean, and the cloth is collected on a roller. This is known as frictioning.

The calender may also be used for plying two sheets together, and for applying a sheet of rubber to frictioned cloth. The latter is done in the same way as

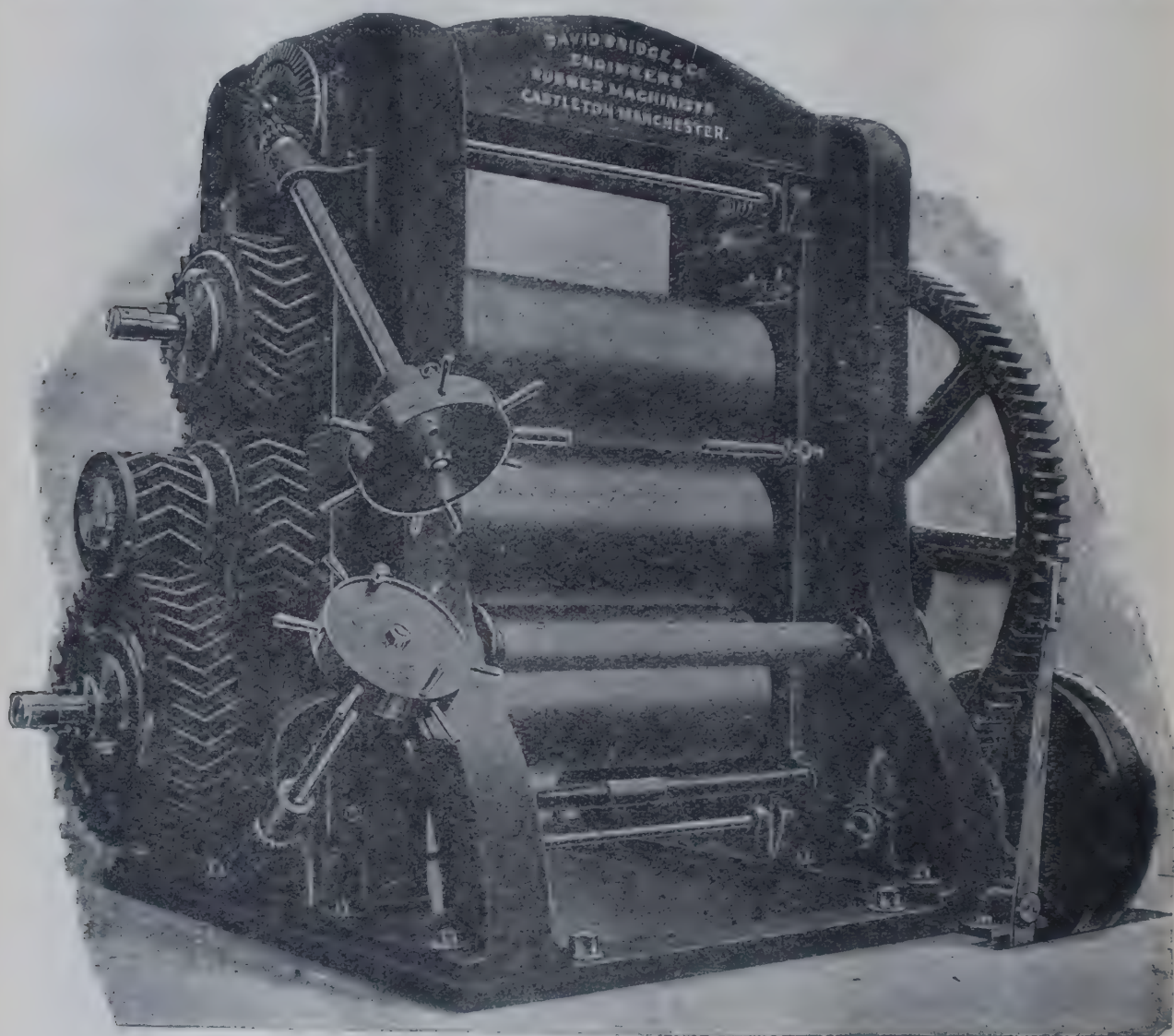


FIG. 163.—Three-Bowl Calender.

frictioning, except that frictioned cloth is passed through instead of cloth, and the rolls all run at even speeds. Plying up is done by mounting the two rolls in cloth at the back of the calender and passing them through the nip set just to press them together. At the same time provision is made to collect the two empty cloths as they unwind.

**Cut Sheet**, which is gradually being displaced by calendered sheet, is employed for tobacco-pouches, etc. The washed and dried rubber is thoroughly masticated, pressed into blocks, frozen in refrigerating chambers, and cut into sheets by rotating the cylindrical blocks against a vibrating knife (analogous to the unrolling of a roll of paper).

**Elastic thread** is cut from calendered sheet, rolled with a fabric into a cylinder after dusting with French chalk, vulcanised, unrolled, coated with shellac solution, wound on a roller, and cut into thread.



**Forcing or Extruding** solid tyres, inner tubes of tyres, tubing, etc., is done in the machine shown in Fig. 164. The warm rubber mixing is fed through a hopper fitted with an automatic roller-feed to a steam-jacketed Archimedean screw, rotated by the gear shown on the left, and is forced through the die shown on the right. This die is provided with a central spike for generating the hollow in tubes, or with a wire to serve as a core in solid tyres, and cables.

**Tyre covers** are usually made up by hand upon a mandrel from proofed



FIG. 164.—Forcing Machine (extrusion).

canvas and calendered sheet; *tyre-tubes* and other *tubing* by building up calendered sheet cut to the desired width; *hose* by building up the cheaper grades by lapping on a mandrel, and by other methods; direct moulding, stamping from calendered sheet, or cutting from cylinders are also used for some kinds of goods.

### De-vulcanisation and Re-manufacture of Rubber

In the “reclaiming” of waste the fibre is usually removed by means of alkali or sulphuric acid, the S by treatment with alkalis, thiosulphate, etc. It has been claimed that some processes remove combined as well as free sulphur. Waste rubber has also been dissolved under pressure in benzene, etc., and utilised in the form of a solution. It is often ground up and used as a filler with raw rubber.



Of late years a new and valuable process, patented by Thomas Gare (Patent Specification, 12,454, A.D. 1906), and modified by Hyatt, Immisch, and others, as described in later specifications, has been invented, by which it is claimed that old and worn rubber articles can be "reformed" and made as good as new without any addition. The process depends upon subjecting the rubber, preferably finely ground, to the action of high pressures, so as to exclude all air from the interstices, and then, whilst the rubber is still under pressure, subjecting it to temperatures above that of vulcanisation. In this process no attempt is made to remove the sulphur. The process depends upon the fact that, when air is excluded, rubber can be subjected to a high temperature, and can even be melted, without destroying its elasticity and compressibility, so long as it is allowed to cool without access of air.

**Rubber Substitutes.**—Many substitutes for rubber have been proposed. The chief depend upon producing from oils, more particularly drying oils, such as linseed oil, an elastic mass by "vulcanising" with S ("brown substitute"),  $S_2Cl_2$  ("white substitute"), or  $Sb_2S_5$  ("red substitute"). These products are known as oil rubber, factis, or white or red substitutes. They are chiefly valuable as cheapening additions for raw rubber.

**Brown Factice** is usually made by heating together rape oil and sulphur; **White Factice** by vulcanising castor oil with sulphur chloride,  $S_2Cl_2$ .

Mixtures of glue or gelatine, and glycerin, oils, or other softening agents, after treatment with tannic acid, chromates, or formaldehyde, have also been used as substitutes for rubber; for example, as cores for tyres and coverings for rollers. "Elastes" belongs to this class.

Cores and fillings for tyres have also been made by injecting into or generating in rubber, gelatine, etc., air or other gases. The inventions of the Pneumatic Tyres Syndicate are of this nature.

## GUTTA-PERCHA

**Gutta-percha** is obtained from the *Isonandra gutta* (East Indies) and other trees, usually by felling the trees and "ringing" the bark at intervals of 12-18 in. The milk which oozes out in the better kinds soon coagulates, and is then boiled alone or with water. In order to clean the product it is reduced, softened in hot water, washed with hot water, strained, masticated between rollers, and sheeted. In the chemical cleansing process small pieces of raw gutta-percha are steeped in caustic alkali or chloride of lime, the latter process yielding a product containing less dirt than the former process. It is sometimes desirable, e.g., in making golf balls, to remove resin from gutta-percha. This is done by extracting the dry material with petroleum spirit, etc., the gutta-percha which remains behind undissolved is then masticated in the usual way. Various processes for extracting gutta-percha from leaves, etc., have been suggested; for example, by means of  $CS_2$ , toluene, etc.

Chemically gutta-percha is closely related to caoutchouc, being in fact, according to Harries, a stereo-isomeride, of formula  $(C_{10}H_{16})_n$ , and, like caoutchouc, it forms an ozonide,  $C_{10}H_{16}O_3$ , which is decomposed by water into laevulinic aldehyde.

Physically, however, there is little resemblance; gutta-percha does not possess elasticity like caoutchouc; but when warmed is extremely plastic, and when pressed in forms gives the finest relief work in exact detail. Gutta-percha at ordinary temperatures is hard but not brittle; it is an excellent electric insulator, and is largely used in the manufacture of electric cables, especially marine ones, because, as compared with rubber, it possesses a greater power of resistance towards water under high pressures.

See also under **Plastics** for a fuller treatment.

## BALATA

**Balata** (from the "bullet" tree or *Sapota mulierii*) is midway in physical characteristics between indiarubber and gutta-percha, and is largely used for



coating canvas for belting, and as a soling for shoes and boots. The milk is obtained by removing the outer bark before tapping, and is coagulated by evaporation or by acetic acid.

**Statistics.**—The accompanying figures give the growth of the world's production of crude rubber (caoutchouc): 1890, 29,330 tons; 1895, 34,827 tons; 1900, 52,864 tons; 1905, 68,879 tons; 1910, 76,553 tons; 1911, 88,000 tons; 1912, 98,950 tons; 1913, 112,000 tons.

The world's production of all grades of rubber in 1911 and the approximate price of these various grades of rubber on 11th May 1912 was as follows:—

	Output in Tons.	Price per lb.*	
		s. d.	s. d.
Amazonas and Brazil (para)	39,000	4 7	10 4 7½
Ceylon and Malaya (plantation)	14,200	4 11	„ 5 0
Africa and the rest of the world	34,800	2 1	„ 4 0
	88,000		

The production of **plantation rubber** was:—1912, 28,500 tons; 1913, 470,000 tons.

It is estimated that the total raw rubber output in 1915-1916 will be nearly 150,000 tons. At present the United States consume one-half the world's output, the United Kingdom and Germany each one-sixth.

*Brazil, Bolivia, and Peru* exported 39,500 tons in 1911, against 40,000 in 1910; in 1912 the export was 43,000 tons, and in 1913, 39,700 tons; *Mexico* in 1911 exported 9,200 tons of guayule; *Ceylon and India* 2,750 tons in 1911; *Malaya* 11,400 tons in 1911; *West African Coast* 15,000 tons in 1911. The exports from the *Straits Settlements, F.M.S., and Ceylon* for 1913 was 71,000,000 lbs., value £11,000,000.

The quantity of caoutchouc imported into England was 30,000 tons in 1906 (value £10,000,000), and 43,800 tons in 1910 (value £26,000,000). The value of the manufactured rubber goods imported into England in 1910 was £627,000, and of the exported was £1,800,000, while the exported **rubber waste** was £356,000. The price of the best Para rubber in 1911 was 6s. per lb. In 1910 it once rose to 13s. a lb. It will probably fall to 2s. per lb. or under in a few years.

The import of **gutta-percha** into the United Kingdom was—1906, 53,000 cwt. (value £489,000); 1910, 97,000 cwt. (value £1,136,000).

It is stated that between 1900-1910 no less than £70,000,000 was expended on rubber plantations. 850,000 acres are under cultivation in the East (1911), and 80 acres in Mexico, Nicaragua, etc.

Estimated yield per tree (Hevea), age 5 years, ½-¾ lb.; 7 years, 1¼-1½ lbs.; 12 years, 3-4 lbs. Some 15-30-year-old trees have yielded 15 to 20 lbs. per tree per year.

Tappings per year—Hevea, 150-160; Castilloa, 4-5. Brazil, Peru, and Bolivia produce about one-half the world's rubber.

\*For modern statistics see Appendix III. The price of rubber varies so widely that these figures are at the moment quite accurate, but prices down to 1s. per pound have been prevalent in the past.





# THE ANALYSIS OF RUBBERS

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Revised by D. E. PARTINGTON, A.I.R.I.

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Raw rubbers contain—1. Dirt, sand, bark; 2. moisture; 3. carbohydrates (sugars of the inosite class); 4. resins; 5. nitrogenous substances (proteins, enzymes); 6. rubber hydrocarbon (caoutchouc); 7. ash.

**The loss on washing** is determined by allowing a stream of water to play on the rubber while it is repeatedly passed through the washing rolls.

By this means the dirt, sand, pieces of bark, etc., are squeezed out of the rubber and carried away by the water, which also dissolves out most of the sugars.

Plantation rubbers are washed before exportation, and for wild rubbers the loss on washing is determined on a large sample in the factory, so the rubber chemist commences his analysis on a sample of the washed and dried rubber.

As acids are used for coagulating the latex on many plantations, and free acid has an injurious effect on rubber, the sample should first be tested for acidity.

**Moisture** may be estimated by placing the rubber in vacuum over sulphuric acid for several days, until the weight is constant, but is more conveniently estimated during the extraction with acetone.

**To estimate the resins**, 2–5 gr. of the rubber are cut into small cubes, or better, the rubber is rolled into a very thin sheet, which is extracted with acetone for six hours in a Soxhlett extractor. Of low grade highly resinous rubbers such as Jelutong, Guayule, etc., 1–2 gr. will be enough.

The acetone extract is brought into a tared flask, the acetone is distilled off in a water bath, and the residue dried in the steam oven for one hour, and then the heating is continued for periods of 15 minutes until the weight is constant. (The drying may be hastened by placing the flask on its side in the steam oven, so that the heavy vapours pour out, and the heating should not be unduly prolonged, as the resins absorb oxygen, so that the weight increases.)

Sometimes a white crystalline ring is observed on the sides of the flask; this is said to consist of sugars which escaped solution during the washing.

The acetone extracted rubber is placed on a watch glass, and dried in the steam oven, or better, in a vacuum oven.

If dried in the air, the rubber should be heated for one hour, and then for periods of 15 minutes, until the weight is constant, or begins to increase. (Acetone extracted rubbers absorb oxygen rather rapidly.)

The difference between the weight lost by the rubber and that of the acetone extract represents the weight of the moisture contained in the rubber.

**Nitrogen** in rubbers is determined by Kjeldahl's method. 1–2 gr. of the rubber are heated on a sand bath with 12 c.c. of conc.  $\text{H}_2\text{SO}_4$ , 8 c.c. of fuming sulphuric acid.

After the acid has been boiling for an hour, 8 gr. of dry  $\text{K}_2\text{SO}_4$  are added, and the heating is continued until a clear, colourless, or pale yellow melt is obtained, or the rubber may be boiled in the sulphuric acid mixture for 3–4 hours; and then a little  $\text{KMnO}_4$  is added cautiously, a few crystals at a time, to the hot acid, and the heating continued until a clear pale yellow liquid is obtained. (Many rubbers contain a little iron, which causes the pale yellow colour.)

The product is then cooled, diluted with 200 c.c. of water, again cooled; 80 c.c. of  $\text{NaOH}$  solution S.G. 1.3–1.4 added, a piece of zinc dropped into the distillation flask, and 100 c.c. of the liquid distilled into 100 c.c. of  $\frac{\text{N}}{10} \text{H}_2\text{SO}_4$ , with the usual precautions.

The excess of  $\frac{\text{N}}{10} \text{H}_2\text{SO}_4$  is titrated with  $\frac{\text{N}}{10} \text{Ba}(\text{OH})_2$ , or  $\text{Na}_2\text{CO}_3$ , using methyl orange as an indicator. The nitrogen figure, when multiplied by 6.25, is usually regarded as representing the amount of proteid in the case of washed rubbers.

**To determine the ash**, about 2 gr. of the rubber are placed in a porcelain crucible (preferably glazed on the inside only), which fits in a circular hole in a piece of asbestos board.



The crucible is heated with a very small Bunsen flame until fumes are no longer evolved, and the carbon deposited on the sides of the crucible is burnt off at the mouth of a muffle furnace, or over a large Bunsen flame. Hevea rubbers (Para, Mollendo, Plantation Para, etc.), may only contain 0.2 per cent. of ash, so in this case about 10 gr. of the rubber should be taken and fumed off, 2 or 3 gr. at a time.

The ash may contain silica, lime, alumina, magnesia, iron oxide, sulphates, phosphates, and chlorine, which are determined by the ordinary methods of analysis. Several methods have been proposed for *the direct estimation of the rubber hydrocarbon*, but this is best determined by difference. The percentage values found for moisture, acetone extract, insoluble organic matter, and ash, when added together and subtracted from 100, give the percentage of caoutchouc contained in the rubber.

**Vulcanised Rubbers.**—Owing to the very large number of both organic and inorganic substances which are introduced into rubber mixings, an exact separation of all the constituents is often very difficult and sometimes impossible.

The following scheme of separation, which is based on the work of Henriques and Weber, is the best which has yet been devised, and may be used for both soft rubbers and vulcanites. The rubber (about 2 gr.) is extracted with acetone for ten hours; this dissolves out rubber resins, free S, and any oils or solid hydrocarbons which the rubber may contain.

The rubber is next extracted with chloroform, for four hours. This extracts part of the tar, pitch and asphalt if present, and part of any reclaim present. If these are present individually, they can be recognised by the dark colour of the bituminous substances, and the light brown of reclaim. If these materials are all present the chloroform extract is not of great value, but it is often possible to say whether or not one or the other is present. If only bitumen is present, this may be determined in the extract by subtracting from the extract expressed as a percentage of the total compound, 1 per cent. of the rubber content, multiplying by 10, and the result is approximately the percentage of tar, pitch, or asphalt present. This is further explained by the following figures of the composition of asphalt after vulcanisation:—

Acetone soluble	-	-	-	-	50
Chloroform soluble	-	-	-	-	40
Insoluble	-	-	-	-	10

It can also be seen that a check on the figure given by chloroform extract can be made by doubling the acetone extract if only asphalt is present.

If only reclaim is present, this can be determined by allowing approximately 40 per cent. to be extracted by chloroform. It is necessary, of course, to have a rough knowledge of the rubber content of the reclaim.

The chloroform extract is of real value in determining the quality of reclaim or, in other words, the degree of reclamation. Winkelmann (*Ind. Eng. Chem.*, 18, 1163 (1926)) has shown that if rubber is completely reclaimed it is 45 per cent. chloroform soluble.

The rubber is then boiled with 50 c.c. of a 5 per cent. alcoholic solution of NaOH for four hours with alcohol in a Soxhlett extractor, and then with water. This removes the factice (rubber substitutes), blown and polymerised oils, with the sulphur and chlorine contained in the factice.

The rubber is then heated in a flask with 60 gr. of a nitronaphthalene for one hour to 180°, cooled, and 150 c.c. of benzene are added.

The liquid is allowed to stand until the insoluble matter settles out, when it is filtered, and the residue washed with benzene, dried, and weighed. In this way the caoutchouc and the sulphur and chlorine combined with it are removed from the mixing. The residue is then extracted with boiling water to remove any starch or dextrine.

The residue may now contain mineral matter, free carbon, fibrous minerals, and sulphur in inorganic compounds.

The free sulphur in the acetone extract may be estimated by heating the dried extract with bromine water and then boiling off the bromine. The liquid is then filtered, acidified with HCl, and the sulphur now present as sulphate is precipitated with barium chloride.

**Mineral oils** usually reveal their presence by imparting a fluorescence to the acetone extract. If waxes are present, the residue from the acetone extract is warmed with 50 c.c. of 96 per cent. alcohol, filtered, and the residue washed with 25 c.c. of alcohol. The filtrate is then cooled to -4°, the wax is filtered and washed with 100 c.c. of 96 per cent. alcohol cooled to -4°.

The figures obtained by weighing the residue left after distilling off the pyridine from the pyridine extract are of doubtful value, as pyridine dissolves some of the rubber, while bitumen is not entirely soluble in pyridine. The sulphur may be estimated by oxidation with HNO<sub>3</sub>, and fusion mixture as described for the acetone extract.

The alcoholic soda extract should be tested for mineral fillers, some of which, such as antimony, sulphide, and zinc oxide, are partially extracted.

**The total sulphur** may be determined by mixing 0.2 gr. of the finely divided rubber or elonite with 6-7 gr. of Na<sub>2</sub>O<sub>2</sub>, and 0.1 gr. of powdered sugar in a nickle crucible, and covering the mixture with a thin layer of Na<sub>2</sub>O<sub>2</sub>.

The crucible is placed in a basin containing a little water, and the mixture is fired by passing a red hot wire through a hole in the crucible lid. The residue is dissolved in the water in the dish, nearly neutralised with HCl, boiled and filtered to remove a few smuts which are formed (the liquid should not be black), acidified with HCl, boiled and precipitated with BaCl<sub>2</sub> as usual.



As  $\text{Na}_2\text{O}_2$  usually contains traces of S, a blank test must be made with the sample used.

By another method the finely divided rubber is heated with a mixture of  $\text{ZnO}$  and  $\text{KNO}_3$  over a spirit Bunsen (to avoid  $\text{SO}_2$ ) gently until the vigorous action is over, and then to a red heat. The product is boiled with  $\text{HCl}$ , filtered, and precipitated with  $\text{BaCl}_2$  as usual.

Cold vulcanised rubbers and white factice (which appears in the alcoholic soda extract) contain chlorine, which may be estimated by precipitating as  $\text{AgCl}$  in the usual manner after the organic matter has been destroyed by ignition with fusion mixture.

The mineral fillers are determined by the usual methods of inorganic analysis, and with the exception of  $\text{Pb}$ ,  $\text{Sb}$  and  $\text{Hg}$  may be estimated in the ash.

$\text{Pb}$  can only occur in black rubbers, and  $\text{Sb}_2\text{S}_5$  is usually put into red rubber mixings, while some special red rubbers owe their colour to vermilion ( $\text{HgS}$ ).

These three metals, which are never introduced together into a rubber mixing, are determined after the organic matter has been destroyed by heating the rubber with nitric acid and ammonium persulphate.

$\text{Pb}$  may be estimated by making the liquid alkaline with  $\text{NH}_4\text{OH}$ , digesting with ammonium acetate, filtering from any insoluble matter ( $\text{SiO}_2$ ,  $\text{BaSO}_4$ ), acidifying with  $\text{CH}_3\text{CO}_2\text{H}$ , and precipitating as  $\text{PbCrO}_4$ .

$\text{Hg}$  and  $\text{Sb}$  are estimated by adding  $\text{HCl}$  to the liquid, diluting and passing  $\text{H}_2\text{S}$  gas.

The  $\text{HgS}$  may be freed from S by extraction with ammonium sulphide, and the  $\text{Sb}$  is best converted into  $\text{Sb}_2\text{O}_4$  by evaporation first with dilute  $\text{HNO}_3$ , then with conc., and finally with fuming nitric acid, when it is ignited and weighed.

### Mechanical Tests

These chemical tests should be supplemented by **Mechanical Tests**, *e.g.*, for elasticity, breaking strength, etc., for which special machines are employed.

It is interesting to note that viscosity measurement is a more accurate test of the strength of rubber than "hand-pulling" or mechanical tensile tests. Schridowitz and Goldsbrough (*Journ. Soc. Chem. Ind.*, 1909, p. 3) used filtered dilute solutions in an Ostwald double-bulb viscometer with pure benzene as solvent, and a temperature of  $20^\circ\text{C}$ . Comparative determinations only are necessary, the viscosity of pure benzene being taken as 1. They showed that a straight line law is obeyed for dense solutions between the viscosity and concentration, and thus by assuming a concentration of 100 per cent. they were able to obtain values for solid matter. These observers conclude that within the same species viscosity measurements vary directly with strength and "vulcanising capacity," and that even when comparing species with species high viscosity indicates strength.

The vulcanisation characteristics should also be investigated by using a range of methods (open cure, press cure, etc.) of time, temperature, and different mixings.

The usefulness of a sample for particular purposes may be ascertained by mechanical tests on best-cure rubber, such as breaking-strain, elongation at break, nature of hysteresis curves, and elongation curves, etc., compression under given load, recovery after compression for fixed time, elasticity (by dropping a steel ball on a sheet of the sample and comparing heights of drop and rebound), abrasion and hardness tests, specific gravity, di-electric strength, effect of reagents on weight, volume, tensile properties, etc., dry heat ( $132^\circ\text{C}$ . for 1 hour), and moist heat (steam,  $160^\circ\text{C}$ . for 3 hours) tests, porosity.

## II.—SYNTHETIC RUBBER

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The term “synthetic rubber” is used to describe products which have rubber-like properties, but do not necessarily possess the same chemical constitution as rubber. Early research aimed at synthesising the rubber molecule from its component materials. The resultant compounds had very poor properties. Nowadays the aim is a synthetic rubber with good properties regardless of the composition of the molecule.

When certain unsaturated hydrocarbons containing the grouping : C : C.C : C : are allowed to polymerise, they form a series of caoutchoucs which possess many of the properties of the best sorts of natural caoutchouc, including the power of vulcanising.

The hydrocarbons from which technical synthetic rubber has been formed are:

**Butadiene** (Erythrene, Divinyl),  $\text{CH}_2 = \text{CH} - \text{CH} = \text{CH}_2$ .

**$\beta$ -Methyl Butadiene** (Isoprene, Methyl Divinyl),  $\text{CH}_2 = \text{C}(\text{CH}_3) - \text{CH} = \text{CH}_2$ .

**$\beta$ - $\gamma$ -Dimethyl Butadiene** (Di-isopropylene, dipropylene),  $\text{CH}_2 = \text{C}(\text{CH}_3) - \text{C}(\text{CH}_3) = \text{CH}_2$ .

**Chloroprene**,  $\text{CH}_2 = \text{C}(\text{Cl}) - \text{CH} = \text{CH}_2$ .

**Butadiene** is at ordinary temperatures a gas.

**Properties of Isoprene** (Methyl Vinyl,  $\beta$ -methyl butadiene).—Colourless liquid with penetrating smell; B.P.,  $36^\circ - 37^\circ \text{C}$ .; density, 0.6804; mol. refract.,  $\text{MR}_D(21^\circ) = 25.45$ ; mol. disp.,  $\text{MD}_{\gamma-a}(21^\circ) = 1.25$ .

**Properties of  $\beta$ - $\gamma$ -Dimethylbutadiene**.—Colourless liquid; B.P.,  $71^\circ \text{C}$ .,  $n_D = 1.43751$ ; mol. refract., 29.65; density ( $20^\circ$ ), 0.7272;  $M_{\gamma-M\alpha} = 1.41$ .

**Properties of Chloroprene**.—Colourless liquid; B.P.,  $59.4^\circ \text{C}$ .; density ( $20^\circ$ ), 0.9583; ref. index, 1.4583.

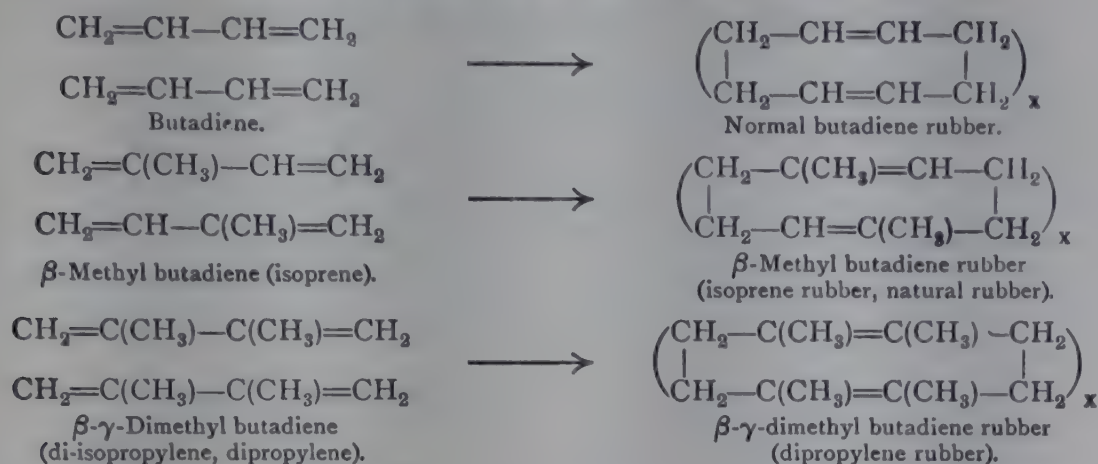
Synthetic rubber is also produced by the co-polymerisation of butadiene with styrene (the famous German “Buna”), and acrylonitrile (Hycar. O.R. Chemigum, etc.).

Finally there are the organic polysulphides (thiokol, perduren, etc.), which have poor physical properties but outstanding oil and solvent resistance.

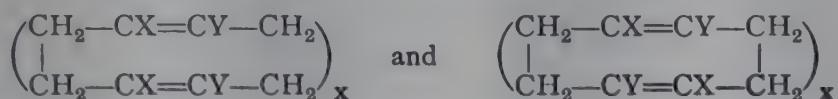
**The higher homologues** of butadiene also produce rubbers; *e.g.*,  $\beta$ -methyl- $\gamma$ -phenyl butadiene (phenyl isoprene),  $\text{CH}_2 = \text{C}(\text{CH}_3) - \text{C}(\text{C}_6\text{H}_5) = \text{CH}_2$ , has been shown to polymerise to a rubber-like body which vulcanised to a product inferior to ebonite.



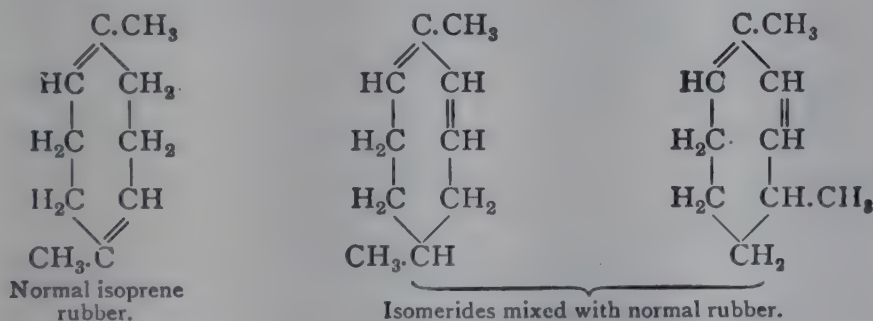
The polymerisation may be regarded as taking place thus:—



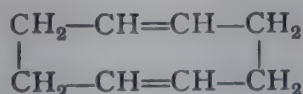
And, in general, a rubber derived from a homologue of butadiene, such as  $\text{CH}_2=\text{CX}-\text{CY}=\text{CH}_2$ , would produce rubbers of the formulæ:—



As a matter of fact the polymerisation is a much more complex matter than this. Thus sticky or liquid lower polymerides are first formed, and the final polymerisation product is formed gradually by further condensation. Moreover, if the polymerisation proceeds too far and the molecules become too condensed, hard brittle products may be formed. Also Harries has shown (*Annalen*, 383, 157-229) that different rubbers are obtained by using different polymerisation agents, *e.g.*, when butadiene is polymerised by heating alone or with acetic anhydride, it yields a "normal butadiene rubber,"  $(\text{C}_8\text{H}_{12})_x$ , while when polymerisation is effected by sodium wire it yields quite a different rubber, called "sodium butadiene rubber." In a similar manner several isomeric rubbers are obtained by polymerising isoprene and dimethyl butadiene respectively. Thus, for isoprene rubber (natural rubber) Harries suggests (*Annalen*, 383, p. 187) the presence of three isomerides, which have the double linkage in a different position, thus:—



Moreover each of these isomerides may have several stereoisomerides. It will be seen that according to Harries' views the basis of rubber is the hydrocarbon cyclopentadiene (1:5) which contains a ring of eight carbon atoms:—



The modern view is in favour of a very long open chain structure.

**Identification of Rubbers.**—Harries has shown that the only way to identify a rubber is to ozonise it, and then decompose the ozonide produced (see p. 358), because simple bodies are thus obtained which yield with phenylhydrazine finely crystalline compounds with sharp melting points, and so can be easily identified, and at the same time give an insight into the structure of the molecule. Although rubbers yield bromides and nitrosites (p. 359) yet these compounds are amorphous without sharp melting points, and so do not afford good means of identifying the various rubbers.

The polysulphides are readily identified, either vulcanised or not, by their strong odour.

Chloroprene, nitrile, and styrene rubbers are fairly easily identified in the unvulcanised state by the presence of chlorine and nitrogen in the former two, and by the odour of styrene in the latter. However, when vulcanised it is almost impossible to detect Buna from natural rubber.

## MANUFACTURE OF BUTADIENE, METHYL BUTADIENE (ISOPRENE), AND DIMETHYL BUTADIENE FOR THE PURPOSE OF MAKING SYNTHETIC RUBBER

Since rubber can be produced quantitatively from butadiene, the problem of successfully producing synthetic rubber commercially resolves itself firstly into the manufacture of butadiene, styrene, chloroprene, or dimethylbutadiene, as cheaply as possible, and secondly, into the polymerisation of these substances to rubber.

### Manufacture of Butadiene (Erythrene, Divinyl)

1. **From Butyl Alcohol** (Fernbach's Fusel Oil).—Perkin (*Journ. Soc. Chem. Ind.*, 1912, 31, 622) converts the butyl alcohol,  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$ , into butyl chloride,  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{Cl}$ , by passing dry  $\text{HCl}$  gas into the heated alcohol, and then chlorinates the butyl chloride so as to produce dichlorides.

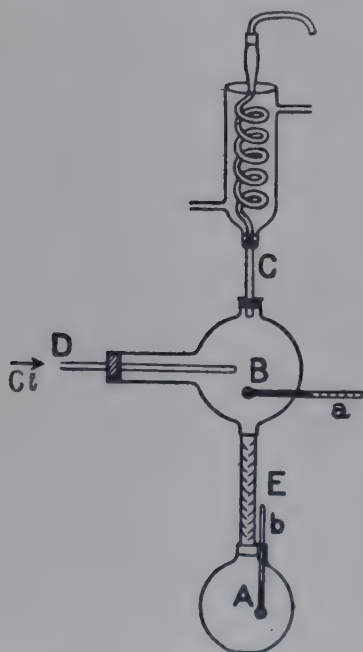


FIG. 164a.

Pim's Chlorinating Apparatus.

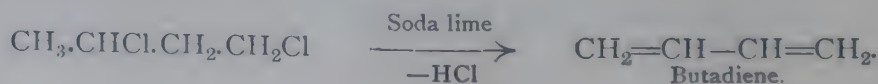
The difficulty that a large proportion of higher chlorides are produced by chlorinating under ordinary circumstances is got over by employing a special apparatus devised by Mr C. A. Pim.

The liquid is boiled in the vessel A (Fig. 164a) until the chlorinating chamber B is full of vapour and the liquid drops from the end of the reflux condenser C. Then a stream of dry chlorine is passed in through D, keeping, however, the butyl chloride in excess. During the chlorination process the apparatus must stand in a good light, and on dull days the ultra-violet light of a mercury lamp is used to facilitate chlorination. As fast as the higher-boiling dichloride is produced in B it drops back into the vessel A; and as this is provided with an efficient fractionating column E, only the lower-boiling butyl chloride can pass up into the chlorinating chamber B; the dichlorides are thus removed from the sphere of action of the chlorine and thus escape further chlorination. The liquid in A is finally fractionated and the dichlorides separated *a* and *b* are regulating thermometers.

There are thus produced the dichlorides



$1 : 4 \text{CH}_2\text{Cl}\cdot\text{CH}_2\text{CH}_2\cdot\text{CH}_2\text{Cl}$ . These dichlorides are then passed over hot soda lime at a temperature of  $470^\circ \text{C}$ ., whereby hydrochloric acid is abstracted and butadiene formed, thus:—



Harries (*Annalen*, 1911, 383, 181) also uses butyl alcohol and produces the bromide  $\text{CH}_3\text{CHBrCH}_2\text{CH}_2\text{Br}$ , which he also passes over heated soda lime.

The commercial success of this method depends upon the production of cheap butyl alcohol. This is obtained by fermenting starchy mashes with **Fernbach's Cultures**, whereby a large yield of fusel oil containing no less than 65 per cent. of butyl alcohol is obtained (see pp. 314, 333).

2. **Butadiene from Aldehyde**.—Perkin (*loc. cit.*) also proposes to obtain butadiene from aldehyde (which is prepared from alcohol, and thus from starch) by treating it with very dilute potassium carbonate whereby aldol,  $\text{CH}_3\text{CH}(\text{OH})\text{CH}_2\text{CHO}$ , is produced. This is reduced and yields 1 : 3-butylene glycol,  $\text{CH}_3\text{CH}(\text{OH})\text{CH}_2\text{CH}_2\text{OH}$ ; this is then converted into 1 : 3-dichlorobutane,  $\text{CH}_3\text{CHCl}\cdot\text{CH}_2\text{CH}_2\text{Cl}$ , by dry  $\text{HCl}$  gas; and finally butadiene obtained by passing this over hot soda lime as above described.

Here the starting point is starch, in the form of potatoes or grain, which are fermented to alcohol, which is then oxidised to aldehyde.

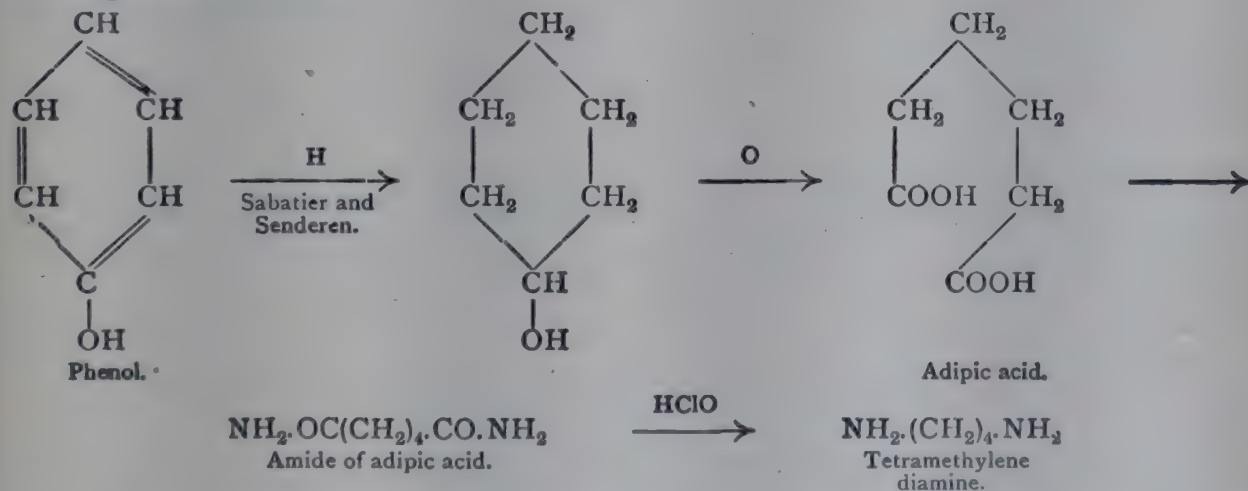


**3. Butadiene from Light Petroleum.**—*Fr. Bayer & Co., Elberfeld*, English Patent, 448, 1912, produce butadiene from cyclohexane and its homologues (derived from light petroleum) by passing the vapours over hot contact surfaces, especially over a spiral of aluminium silicate heated electrically to a dull red heat. The unchanged hydrocarbon is returned to the boiler, whilst the gases are freed by cooling from liquid hydrocarbons and the butadiene extracted from them. In their French Patent, 437,387, 1911, they decompose petroleum or its fractions or residues by means of hot contact surfaces, *e.g.*, a fraction of B.P.  $70^{\circ}$ – $100^{\circ}$  C., obtained from Caucasian petroleum, is passed in a state of vapour over a coil of platinum heated electrically to dull redness. The unaltered petroleum is returned to the container, whilst the gases are freed from low boiling hydrocarbons by cooling, and the butadiene is isolated either by strong compression and cooling and fractionating, or by a chemical process such as converting it into its tetrabromide. *Perkin and Weizman* (English Patent, 9,722, 1911) pass 1:2-butylene,  $\text{CH}_3\text{CH}_2\text{CH}:\text{CH}_2$  (obtained by cracking petroleum), over heated finely-divided copper, whereby a mixture of butadiene,  $\text{CH}_2:\text{CH}:\text{CH}:\text{CH}_2$  (by removal of H), and unchanged butylene results. The butadiene is then polymerised, and the unchanged butylene distilled off from the resulting caoutchouc.

**4. Butadiene from Phenol.**—*Fr. Bayer & Co.* (English Patents, 8,100, 1910; 18,935, 1911) produce butadiene by treating tetramethylenediamine,  $\text{NH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2$ , with water and KOH, then adding methyl iodide,  $\text{CH}_3\text{I}$ , in small portions, when we get formed tetramethylenehexamethyl diamine iodide,  $(\text{CH}_3)_3\text{IN}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2\text{N}(\text{CH}_3)_3\text{I}$ . This is converted into the hydroxide  $(\text{CH}_3)_3(\text{OH})\text{N}-(\text{CH}_2)_4-\text{N}(\text{CH}_3)_3(\text{OH})$  by silver oxide. When this is warmed it decomposes into butadiene, thus:—



This is really a method of preparing butadiene from coal-tar through phenol by means of the following series of reactions:—



**5. Butadiene from Acetylene.**—*Heinemann* (English Patent, 20,772, 1908) produces butadiene by heating acetylene and ethylene together in a tube heated to dull redness, thus:—



In the early days of synthetic rubber isoprene was the raw material used for polymerisation. This was due to the fact that the prevalent idea was that a synthetic rubber must be chemically the same as natural rubber. Himly; Williams (*Proc. Royal Soc.*, 1860, x., 516); Bouchardat (*Bull. Soc. Chem.*, 1875, xxiv., 108); Tilden (*Chem. News*, 1882, xli., 120) had all shown that rubber was composed of isoprene, and that the latter could be polymerised to a rubber-like substance.

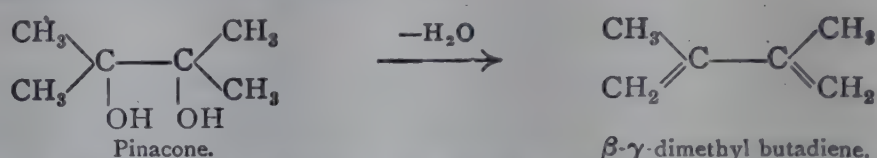


Isoprene rubber has very poor properties, and synthetic rubber would never have reached its present important position had not ideas changed about 1910, when the old synthesis method was dropped in favour of building up any molecule which had rubber-like properties.

### Manufacture of $\beta$ - $\gamma$ -Dimethyl butadiene (Di-isopropenyl, Dipropylene)

(See Couturier, *Ann. Chim. Phys.*, **26**, 485 (1892); *Bull. Soc. Chim.* (3), **33**, 454 (1880); Kondakow, *Journ. Prakt. Ch.* (2), **59**, 299 (1899); **62**, 175 (1900), **63**, 113 (1901), **64**, 109 (1901). See also German Patent, 57,466, iv. 12, of the Badische Anilin- u. Soda-Fabrik, and English Patent, 2,312, 1912, of Fr. Bayer & Co., Elberfeld.)

This substance has technical importance, since Kondakow showed that it can be polymerised into a caoutchouc which is capable of vulcanisation, producing an elastic sheet of good firmness.  $\beta$ - $\gamma$ -dimethyl butadiene can be prepared from Pinacone,  $(\text{CH}_3)_2\text{C}(\text{OH})-\text{C}(\text{OH})(\text{CH}_3)_2$ , e.g., by heating with dilute sulphuric acid (Couturier), or by heating pinacone dichloride with alcoholic potash (Kondakow). Technically the best way is to lead pinacone over heated potassium bisulphate (German Patent, 57,466, 1912), according to the patented method of Meisenburg and Delbrück (Fr. Bayer):—



Pinacone is obtained from Acetone by reducing it with magnesium amalgam (Holleman, *Rec. des Pays Bas*, **25**, 206 (1906); *Zentralbl.*, 1906, ii. 748):—



**Manufacture of styrene (vinylbenzene).**—Styrene is prepared by the dehydrogenation of ethylbenzene. Ethylbenzene is generally prepared by direct synthesis from benzene and ethylchloride. Under the action of aluminium chloride as catalyst, benzene and ethylene also combine to form ethylbenzene. This is at cracked high temperature (800°–950° C.). According to one process, when carried out between 500°–600° C. with suitable catalyst, a yield of 35 per cent. styrene is obtained.

Ethylbenzene is also obtained in small quantities as a by-product from petroleum refining.

**Manufacture of Chloroprene.**—Acetylene is polymerised into monovinyl acetylene by passing through highly concentrated cuprous and ammonium chloride catalysts. Monovinyl acetylene is then converted into 2-chloro-1,3-butadiene by treating with cuprous chloride catalyst and hydrochloric acid.

### Manufacture of Synthetic Rubber by Polymerising Butadiene, Isoprene and its Homologues

Butadiene, isoprene and its homologues can be polymerised into caoutchouc-like bodies by a great many methods, all of which are protected by patents.

**1. Polymerisation by Metallic Sodium.**—Polymerisation of the whole mass of butadiene or isoprene by the catalytic action of small quantities of sodium at a low temperature was discovered independently by Dr Matthews and C. Harries in 1910. The action is practically quantitative, and is not seriously affected by the presence of impurities like trimethylethylene,  $(\text{CH}_3)_2\text{C}=\text{CH}\cdot\text{CH}_3$ , which are not capable of polymerising to rubber.

In order to polymerise the isoprene to rubber it is sealed up in tubes with about 3 per cent. of thin sodium wire, and heated for several days at about 60° C. The dark brown product may be treated with acetone, which precipitates the rubber, and this may then be washed with alcohol or treated with steam to remove any unpolymersed hydrocarbon. Harries (*Liebigs Annalen*,



1911, 383, 213) showed that when butadiene was heated in a closed tube to 35°–40° C., with about 5 per cent. of sodium wire it similarly polymerised to produce an excellent rubber. From 9 g. butadiene he obtained 8 g. butadiene rubber—a practically quantitative yield—which could be vulcanised by either the hot or cold process.

Since the action is catalytic, the bulk of the sodium is recovered unchanged. The method is, technically, a very important one.

**2. Polymerisation by Heating.**—Butadiene, chloroprene, and butadiene/styrene, etc., mixtures can be polymerised by heating under pressure. Pressure is necessary to keep butadiene liquid since it is a gas at atmospheric pressure. However, polymerisation in the mass is not carried out nowadays. Polymerisation in the emulsified state has shown that most of the defects (smell, colour) of the early synthetics were due to polymerisation in the mass.

**3. Polymerisation by Saturating with Oxygen or Ozone.**—Heinemann (English Patent, 14,041) treats the cold isoprene with oxygen or ozone for some hours, and then heats the oxidised product in a closed vessel from 40°–100° C. for many hours until the isoprene becomes viscous. The vessel is cooled and the mass freed from unconverted liquid by evaporating and precipitating the caoutchouc with alcohol.

**4. Other Methods of Polymerising.**—Sunlight, concentrated HCl, alkalis, and other similar chemicals promote polymerisation. Blood serum, albumin, starch, urea, etc., also polymerise butadiene.

**5. The modern method of polymerisation is in the emulsified state.** Emulsion polymerisation can be much more easily controlled and is not exothermic. The reaction can be instantly stopped at any desired stage by the introduction of an inhibitor. It is by this means that the desired properties are obtained in synthetic rubbers.

Nowadays it is rare to find one monomer polymerised on its own. Co-polymerisation is nearly always employed. In this way butadiene is co-polymerised with styrene (Buna, G-R-S) or acrylonitrile (Hycar, O.R., Perbunan), or isobutene (butyl rubber).

The monomers, if gaseous, are liquefied by pressure and then emulsified by the use of such substances as sodium oleate, sodium stearate, sulphonated mineral oils, organic sulphonic acids, saponin, etc. An emulsion stabiliser, such as casein, glue, albumen gelatin, gum arabic, is also added. Catalysts for the polymerisation reaction are also added. Examples of these are benzoyl peroxide, hydrogen peroxide, persulphates and percarbonates. A regulator to control the amount of side branching is necessary. Very little is known of how these substances work, but experience has shown that chlorinated hydrocarbons, like carbon tetrachloride, are useful in this respect. Finally, the whole emulsion must be brought to a pH of 6.5.

Polymerisation is now brought about by raising the temperature and keeping the emulsion violently agitated. When polymerisation has proceeded to a sufficient degree, phenyl-beta-naphthylamine is added to stop the reaction. The rubber is then obtained by coagulation. The following substances may be used to bring this about: aluminium chloride, ferric chloride, calcium chloride, barium chloride, acetone, ethyl alcohol.

Example of an emulsion formula:

Butadiene	-	-	-	60–75.
Styrene	-	-	-	40–25.
Emulsifying agent	-	-	-	1–5.
Polymerisation catalyst	-	-	-	0.1–1.0.
Regulator	-	-	-	0.1–1.0.
Stabiliser	-	-	-	1–5.
Water	-	-	-	100–250.





## SECTION X

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# The Industry of Aliphatic Chemicals





# THE INDUSTRY OF ALIPHATIC CHEMICALS

By G. MARTIN, Ph.D., D.Sc.

With slight additions by E. I. COOKE, M.A.(Cantab.), B.Sc., A.R.I.C.

## ALIPHATIC ACIDS

### Oxalic Acid, $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$

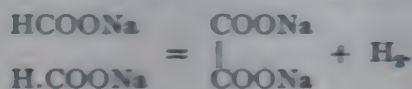
UNTIL recently oxalic acid was obtained exclusively from sawdust (or other carbohydrate) by heating to  $240^\circ$ - $260^\circ$  for about six hours in iron pans with caustic alkali (40 parts KOH + 60 parts NaOH), usually in the proportion 50 parts wood to 100 parts alkali. On cooling, the material was thrown into iron filter boxes with wire-gauze false bottoms, and the substance washed with water drawn through the mass by means of a vacuum pump. The residue of sodium and potassium oxalate was heated while stirring with milk of lime in an iron pan, the caustic soda formed was drawn off and used again, while the insoluble calcium oxalate, after washing, was decomposed by dil.  $\text{H}_2\text{SO}_4$  in wooden lead-lined tanks, and purified by recrystallisation.

Recently (German Patent, 103,856) the heating has been carried out *in vacuo* at  $180^\circ$  C.—a much lower temperature. Another process (A. Droste, German Patent, 199,583) mixes the sawdust, etc., with half its weight  $\text{Na}_2\text{CO}_3$  solution (sp. gr. 1.04-1.1), adds KOH solution of same specific gravity, stirs, and rapidly adds the theoretical amount (determined by a previous experiment) of powdered permanganate, stirs, allows to stand twelve to twenty hours, when the wood is almost completely oxidised to oxalic acid.

**Manufacture of Oxalic Acid from Formates.**—The recent synthetic methods of manufacturing formic acid has so lowered the price of formates that the synthetic manufacture of oxalic acid from them has become profitable, and has largely displaced the older method. When sodium formate is heated to  $360^\circ$  (German Patent, 111,078) with sodium carbonate it produces sodium oxalate, thus:—



German Patents, 144,150, 161,512, 204,895, taken out by the Elektrochemische Werke, Bitterfeld, allow a better and almost theoretical yield of oxalate by mixing sodium formate with sodium oxalate and about 1 per cent. of alkali, and heating, when, apparently, the formate decomposes catalytically, thus:—



The formate first melts, hydrogen is evolved, and at  $360^\circ$  C. the mass solidifies again to a mass of technically pure oxalate in a porous condition. By heating *in vacuo* the change occurs at  $280^\circ$  C., and the evolved hydrogen is pumped off as fast as it is generated and used for heating purposes, etc. At the low temperatures employed there is no danger of explosion since the evolution of gas ceases instantly when the vacuum is broken.

The Acid Oxalates of Potassium (salts of sorrel, salts of lemon,  $\text{KHC}_2\text{O}_4$  and  $\text{KHC}_2\text{O}_4 \cdot \text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ ) are made by adding potassium carbonate to a suitable amount of oxalic acid and crystallising. Valuable domestic detergents.

**Antimony Potassium Oxalate**,  $\text{K}_3\text{Sb}(\text{C}_2\text{O}_4)_3 \cdot 6\text{H}_2\text{O}$ , is used as a substitute for tartar emetic in calico printing.

**Uses.**—Acid potassium oxalate,  $\text{COOH} \cdot \text{COOK} \cdot \text{H}_2\text{O}$ , is much used as a mordant for cloth printing and dyeing; oxalic acid itself is used for whitening leather, for metal polishing powders, for removing ink-stains and iron mould from cloth, for bleaching stearine and straw (for hats), for dissolving Prussian blue in ink-making (see **Inks**), etc. etc.

**Statistics.**—The German exports of oxalic acid and salts are shown by the following figures: 1909, 44,709 dz.; 1908, 51,787 dz.; 1907, 46,827 dz.\*

Of these amounts the following countries received:—

	1909.	1908.	1907.
	Dz.	Dz.	Dz.
U.S.A. - - - - -	20,850	26,368	20,681
Great Britain - - - - -	5,478	4,578	8,111
France - - - - -	4,224	5,351	4,241

The German import in 1909 was only 17 dz.

The United States imported in 1910, 4,833,000 lbs. (value \$280,000), and in 1909, 9,800,000 lbs. (value \$621,000).

For modern statistics see Appendix III.

### Formic Acid, $\text{H} \cdot \text{COOH}$

Formerly formic acid was obtained by heating oxalic acid with glycerol. It is now prepared exclusively by passing carbon monoxide (CO) under 6–7 atmospheres over a mixture of calcined sodium carbonate and dry slaked lime, heated to  $100^\circ\text{--}170^\circ\text{C}$ .: †—



**Goldschmidt's** process consists in heating sodium hydroxide to  $150^\circ\text{--}170^\circ\text{C}$ . with carbon monoxide under 6–7 atmospheres pressure. Yield theoretical.

To obtain the free acid the sodium formate was formerly distilled with concentrated sulphuric acid, whereby much acid was destroyed. It has been recently proved (German Patent, 193,509) by the Chemische Fabrik Grünan, Landshoff and Meyer, that acid sodium sulphate,  $\text{NaHSO}_4$ , may replace the sulphuric acid with advantage, since it does not decompose formic acid, and is a cheap by-product of the alkali industry. The technical sodium formate is thoroughly mixed with finely powdered sodium bisulphate,  $\text{NaHSO}_4$  (95 per cent.), and heated in retorts provided with stirring apparatus. A 97–98 per cent. formic acid distils over, while there remains in the retort a mass of finely powdered normal sodium sulphate,  $\text{Na}_2\text{SO}_4$ . Aqueous solutions of formic acid are concentrated by distillation in columnar stills. A special still for continual distillation has recently been patented by Hamburger (German Patent, 206,902).

**Anhydrous Formic Acid** is prepared from dilute aqueous solutions by neutralising with lead carbonate, drying the lead formate, and decomposing in retorts (heated by hot water to  $100^\circ\text{C}$ .) in a stream of  $\text{H}_2\text{S}$ .  $\text{PbS}$  remains behind

\* 1 dz. = 100 kg. =  $\frac{1}{16}$  ton.

† German Patents, 212,844, 179,515, 209,417, 212,641.



and anhydrous formic acid distils over, containing some dissolved  $H_2S$ , from which it is freed by redistilling over lead formate. Distilling Na formate with  $NaHSO_4$ , as described above, yields an almost 100 per cent. formic acid.

**Uses.**—Since its cheapened production, its use in industry increases rapidly, as it combines the properties of an aldehyde, a moderately strong acid, and a powerful reducing agent. It can consequently be used for a great many different purposes. It finds its chief application in the dyeing industry (especially in wool dyeing) where it is replacing acetic and lactic acid, and acid potassium tartrate (argol). Large quantities of formates are now used for making oxalic acid. It is also used as an antiseptic for preserving fruit juices; in brewing it is added to the mash, where it stimulates the fermentative power of the yeast, preserves the diastase in the malt, and prevents certain acid-producing bacteria from developing; also used in tanning.

**Statistics.**—The United States imported in 1909, 809,000 lbs. (value \$57,000), and in 1910 770,000 lbs. (value \$54,000) of formic acid.

For modern statistics see Appendix III.

For **Acetic Acid** see under **Vinegar** and under **Wood Distillation**.

### Tartaric Acid, $COOH.CH(OH).CH(OH).COOH$

#### LITERATURE

RASCH.—“Die Fabrikation der Weinsauer.” Berlin, 1897.

STIEFEL.—“Das Raffinieren des Weinstein und die Darstellung der Weinsteinsäure.” Vienna, 1894.

DAMMER.—“Technologie der Neuzeit.” Bd. I., 662. 1910. (Dr Emde.)

ALLEN.—“Commercial Analysis.” Vol. i. 1909.

Four varieties of tartaric acid exist, viz., dextro, laevo (which rotate the plane of polarised light to the right or left, respectively), optically inactive racemic acid (decomposable into the above acids), optically inactive mesotartaric acid (not so decomposable).

The only important commercial variety is the dextro-rotatory variety—ordinary tartaric acid.

**Manufacture of Tartaric Acid from Wine Lees.**—Formerly the main raw product for the manufacture of tartaric acid was crude **Argol** or **Tartar**—the potassium salt of tartaric acid. Now the greater part is made directly from the wine lees itself. In the winter months there gradually settles out at the bottom of the fermenting wine vats a deposit consisting of yeast cells, acid potassium tartrate, grape husks, etc. etc. When the wine is run off this mass is removed, pressed between filter cloths to remove excess of wine, then rapidly dried either in simple drying chambers, or in the air itself. It is then sold to the tartaric acid factories.

The composition of lees is greatly altered by the habit, prevalent in Spain, of “plastering” the wine by adding to the wine an impure calcium sulphate, whereby the tartrate is converted principally into **calcium tartrate**, instead of remaining as acid potassium tartrate.

The composition of some typical wine lees, as imported for manufacture, is shown by the following table by Warington:—

## WINE LEES.

	Spanish Wine Lees. I.	Spanish Wine Lees. II.	French Wine Lees.
Tartaric acid as acid tartrate - -	5.27	22.66	4.48
Tartaric acid as neutral tartrate - -	19.13	11.67	21.34
Total tartaric acid - - -	24.40	34.33	25.82
Water (at 100° C.) - - -	10.694	9.750	11.305
Sand - - -	4.900	4.600	4.600
Alumina - - -	0.832	0.578	0.844
Iron oxide - - -	0.351	0.214	0.394
Lime - - -	10.600	4.514	10.567
Magnesia - - -	0.363	0.209	0.327
K <sub>2</sub> O - - -	2.123	...	1.868
Na <sub>2</sub> O - - -	0.060	...	0.100
P <sub>2</sub> O <sub>5</sub> - - -	0.486	0.569	0.527
CO <sub>3</sub> - - -	0.388	...	0.435
Anhydrous tartaric acid - - -	21.472	30.210	22.721
Organic matter - - -	34.448	33.672	37.952

The great difficulty in working wine lees for tartaric acid arises from the fact that a slimy mass is produced on adding water or acid, which renders filtration difficult. Again only small amounts of tartaric acid (22-30 per cent.) are present, and consequently a very bulky residue remains after extracting the tartaric acid. The method now most largely used is **Rasch's Neutral Process** (German Patent, 92,650).

The liquid or pasty lees is placed in a rotating closed cylindrical chamber A, which is heated externally by a steam jacket to 100°-120° C. Within it are a number of heavy balls K, thus giving the chamber the function of a ball mill. The lees are dried by the heat, and all bacteria and spores killed; at the same time the rolling balls grind it up into a fine dust, while any wine or volatile oils present in the lees distil away through the pipe B and may be recovered, or if evil smelling,

burnt in a furnace. The process takes three hours.

The dry powdered lees are now placed in a wooden vat provided with stirring apparatus, cold water from a previous operation is added (1,500-1,800 kg. lees require 80 hl. water), and the whole is well stirred; next the calculated amount of calcium chloride

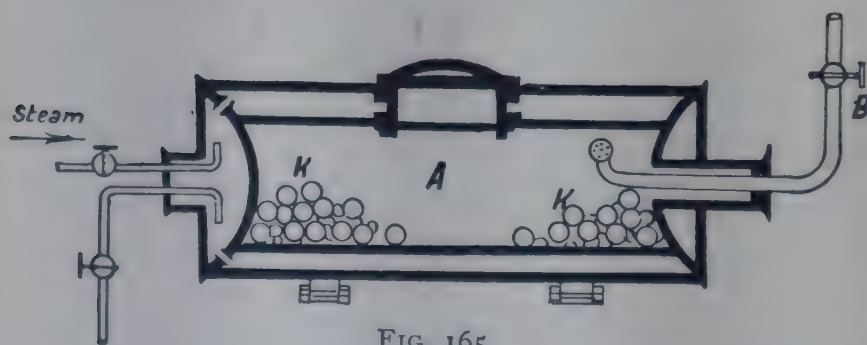


FIG. 165.

solution necessary to form an insoluble calcium salt with the tartaric acid is run into the rapidly stirred mass, and then lime water gradually run in until the solution is exactly neutralised, which is tested with litmus. The process of neutralisation takes three hours. The temperature must not exceed 25° C. After stirring for a couple of hours longer the precipitate of calcium tartrate is allowed to settle, and the supernatant water drawn off. More water is added, the whole mass stirred up again for one hour, allowed to settle, and again the water is drawn off. This process is repeated eight times or so. The precipitate now left in the vat has added to it sufficient sulphuric acid to decompose all the calcium tartrate present, and in addition to provide an acid solution, which prevents fermentation of the acid:— $\text{CaC}_4\text{H}_4\text{O}_6 + \text{H}_2\text{SO}_4 = \text{CaSO}_4 + \text{C}_4\text{H}_6\text{O}_6$ .

The solid and liquid contents of the vat are then passed through the filter press; the expressed fluid, of sp. gr. 10° Bé., containing the free tartaric acid is run into



crystallising pans, and there evaporated for tartaric acid. The first washings of the pressed cake are usually added to the tartaric acid filtrate and evaporated with this. The second wash water, however, is run back into the vat and used with a fresh lot of lees.

If the colouring matter of the wine lees has been previously rendered insoluble by treating the moist lees with 1-2 per cent. of formaldehyde and drying as above, the mother liquors yield on evaporation the first time a crop of white crystals (German Patent, 194,812). The first evaporation is carried out in large wooden vessels lined with lead, heated by leaden steam pipes, and provided with stirring apparatus. The liquid is concentrated to 25° Bé., the precipitated  $\text{CaSO}_4$  is filtered off, and the tartaric acid allowed to crystallise. All mother liquors over 25° Bé. must be concentrated in vacuum evaporators as not only is heavy loss avoided but better products of crystallisation are attained; the mother liquors when sufficiently concentrated are run out into large crystallising pans. The mother liquors for crystallising should contain 60-90 g.  $\text{H}_2\text{SO}_4$  per litre. When necessary the mother liquors are decolourised with bone charcoal (previously extracted with  $\text{HCl}$ ) and potassium ferrocyanide. Sometimes, but only in exceptional cases,  $\text{H}_2\text{S}$  or  $\text{CaS}$  is added to get rid of lead. When the tartaric acid is for edible purposes evaporation is carried out in earthenware vessels, thus avoiding the introduction of lead into the product.

**Manufacture of Tartaric Acid from Argol, Crude Tartar, or Cream of Tartar.**—Before the method of working wine lees for tartaric acid was understood, almost all the tartaric acid of commerce was obtained from this source. It is now principally used for making potassium tartrate.

**Argol** or crude tartar is the crystalline crust deposited on the sides of the vessels used for fermentation. It contains 40-70 per cent. tartaric acid, principally as potassium hydrogen tartrate,  $\text{KH.C}_4\text{H}_4\text{O}_6$ . Its deposition is favoured by the fact that the salt is but sparingly soluble in dilute alcohol. Very low grade **Argols** resemble superior wine lees, while best quality **Argols** may equal ordinary refined tartar. **Cream of tartar** or refined tartar is obtained by boiling crude argol with water, filtering, and crystallising.

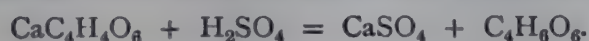
To obtain tartaric acid the crude tartar is boiled with water containing chalk, whereby half the tartaric acid is converted into insoluble calcium tartrate:—



Calcium sulphate is then added, whereby the remainder of the tartaric acid is precipitated as calcium tartrate:—



The precipitated calcium tartrate is strained through a sieve, filter pressed, washed, and converted into tartaric acid by treating with sulphuric acid, the  $\text{CaSO}_4$  being deposited and the solution of tartaric acid being drawn off and boiled down for tartaric acid crystals as previously described:—



**Properties.**—Ordinary tartaric acid is soluble in 0.7 part of cold water and 0.5 part of boiling water; its aqueous solutions are gradually decomposed from the growth in them of fungus. Calcium sulphate, lead, and free sulphuric acid may be present in commercial tartaric acid.

**Uses.**—By far the largest quantity of tartaric acid is consumed in the dyeing and calico-printing industries, being there used as a mordant, especially in the form of tartar emetic,  $\text{KC}_4\text{H}_4(\text{SbO})\text{O}_6$ . It is also used for effervescing medicines, baking powders, etc., also as a preservative for albumen, glue, gelatine, jellies, etc., for medicines, and for making chrysamine.

**Tartar Emetic, Potassium Antimonytartrate**,  $\text{K}(\text{SbO})\text{C}_4\text{H}_4\text{O}_6\frac{1}{2}\text{H}_2\text{O}$  made by making 3 parts of  $\text{Sb}_2\text{O}_3$  and 4 of cream of tartar into a thin paste with water, digesting on the water bath for thirty minutes, adding 8 parts of water, boiling, and filtering while hot. Octahedral crystals, soluble in 14.5 parts of cold and 1.9 parts hot water. Used as a mordant in dyeing and calico printing, also in medicine.

**Statistics.**—The German import of tartaric acid amounted to: 1909, 3,241 dz.; 1908, 2,816 dz.; 1907, 2,525 dz.

In the same time she exported: 1909, 19,076 dz.; 1908, 17,259 dz.; 1907, 15,289.

Great Britain received of this amount: 1909, 11,260 dz.; 1908, 9,484 dz. (1 dz. = 100 kilos = about  $\frac{1}{16}$  ton).

The total import of tartaric acid and cream of tartar into Great Britain is shown by the following figures:—

**Tartaric Acid.**—1906, 36,779 cwt.; 1910, 44,584 cwt.; value in 1910, £203,365.

**Cream of Tartar.**—1906, 64,287 cwt.; 1910, 81,983 cwt.; value in 1910, £307,000.

The export from Great Britain in 1910 was 2,000 cwt. (value £8,000) of cream of tartar, and 7,600 cwt. (value £31,000) of tartaric acid.

The United States imported in 1910, 28,400,000 lbs. (value \$2,232,000) of tartar, and 104,000 lbs. (value \$16,000) of tartaric acid.

**Citric Acid**,  $\text{COOH.CH}_2\text{C}(\text{OH})(\text{COOH}).\text{CH}_2.\text{COOH}$ ,

Occurs in the acid juices of many fruits; it is obtained commercially from the lemon, the lime, and the bergamot by pressing the fruit, concentrating the



expressed juice, heating nearly to boiling and running in, with constant stirring, a mixture of chalk and water. Calcium citrate is formed, and being more difficultly soluble in hot than in cold water, is precipitated. After filtering and washing, the crude calcium citrate is then decomposed with sulphuric acid similarly to the calcium tartrate in the manufacture of tartaric acid. Expressed lemon juice is a practically pure solution (6 per cent.) of citric acid and is the best raw material. The juice, however, is concentrated to 60 per cent. citric acid before treating with chalk.

The following table (after Warrington) shows the amount of acid met with in the various citric juices which occur in commerce :—

	Specific Gravity.	Acid.	Combined Organic Acid.
		Oz. per Gallon.	Oz. per Gallon.
Lemon juice, raw - - -	1.035-1.040	10.6-13.5	0.4-0.7
„ concentrated - - -	1.28-1.38	82-112	8-6
Lime juice, raw English - -	1.04-1.05	11-13	0.3
„ raw Sicilian - - -	...	6-9	0.85
„ concentrated - - -	1.20-1.25	56-72	6-8
Bergamot juice, concentrated -	1.22-1.25	47-55	7-8

It is interesting to note that an organism, *Mucor piriformis* (see German Patent, 72,957, C. Wehmer), is known which ferments sugar directly into citric acid; lemon juice, however, is produced so cheaply in Sicily that no wide technical application of this fact has yet been made.

Citric acid was formerly frequently adulterated with the cheaper tartaric acid. For detection of the adulteration see Allen's "Commercial Analysis," vol. i. p. 588 (1909).

Commercial citric acid often contains sulphuric acid and lead. To free from lead it is treated with  $H_2S$ , completing the crystallisation in non-lead vessels.

**Properties.**—Crystallises in colourless prisms with 1 molecule  $H_2O$ . Dissolves in three-fourths part of cold water or one-half part of hot water; melts,  $70^{\circ}$ - $75^{\circ}$  C.

**Statistics.**—German imports: 1909, 3,990 dz.\*; 1908, 5,537 dz.; 1907, 4,481 dz. German exports: 1909, 3,668 dz.; 1908, 4,537 dz.; 1907, 3,566 dz.

The quantity of lime and lemon juice imported into Great Britain in 1910 was: 685,557 gals. (value £84,455).

The United States in 1910 imported 142,000 lbs. (value \$41,000) of citric acid, lemon and lime juice to the value of \$65,000, and no less than 4,140,000 lbs. of calcium citrate (value \$568,000).

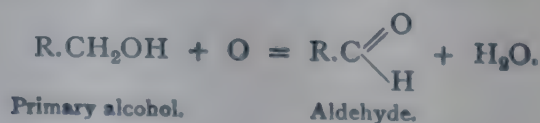
For modern statistics see Appendix III.

For the manufacture of Lactic and Butyric Acids see under Fermentation Industries, p. 315.

## Preparation of the more common Aliphatic Chemicals

### II. ALDEHYDES

Aldehydes are produced by oxidising primary alcohols: thus:—



Of the numerous aldehydes known we will only consider two, viz., Formaldehyde and Acetaldehyde.

\* 1 dz. = 100 kilos = about  $\frac{1}{4}$  ton.



# Formaldehyde, H.CHO,

Is at ordinary temperatures a pungent smelling gas condensing to a colourless liquid at  $-21^{\circ}\text{C}$ . It usually occurs in commerce either dissolved in water, when the solution is called "**Formaline**," or else in a solid polymerised form,  $(\text{HCHO})_3$ , known as "**Trioxymethylene**."

**1. Manufacture from Methyl Alcohol.**—The aqueous solution (35-40 per cent.) is usually made by passing a mixture of methyl alcohol vapour and air, obtained by warming the methyl alcohol to  $50^{\circ}$  and drawing a rapid stream of dry air through it over "contact" substances, such as platinum, coke, copper salts, unglazed porcelain, etc., maintained at a low red heat. The methyl alcohol is oxidised to formaldehyde. The vapours pass into a number of condensing chambers arranged in series; in the first two chambers, which are empty, a 35-40 per cent. solution of formaldehyde ("formaline") is deposited, which may be freed from a little unchanged methyl alcohol by distillation.

In the other condensers a very weak aqueous solution of formaldehyde collects which is ultimately brought up to the correct strength by the passage of the methyl alcohol vapour. The reaction is:— $\text{CH}_3\text{OH} + 2\text{O} = \text{H.CHO} + \text{H}_2\text{O}$ .

**2. Manufacture from Methane Gas.**—Several patents have been taken out for manufacturing formaldehyde cheaply from marsh gas, coal gas, coke-oven gas, or in fact any gas containing a considerable amount of methane.

G. Glock's Patent (German Patent, 109,014) consists in passing a mixture of methane,  $\text{CH}_4$  (or a gas containing methane, such as coal gas), and air or oxygen in amount insufficient for complete combustion over red-hot "contact" agents, such as pumice, copper, asbestos, etc., a mixture of pumice and copper being especially efficient. The *Sauerstoff- und Stickstoff-industrie Hansmann & Co.* (German Patent, 214,155) use as the "contact agent" merely bark (either in lumps or ground), tar, or similar material. Here the temperature of formation is reduced from the  $600^{\circ}\text{C}$ . or so, necessary in the case of other contact agents, to  $30^{\circ}$ - $50^{\circ}\text{C}$ . The yield is 4.7 per cent. of theory, and it is proposed to use waste natural gas for the purpose. Methyl alcohol and formic acid are simultaneously produced.

*Moest* (German Patent, 138,442) electrolyses a solution of sodium acetate and sodium perchlorate, and obtains at the anode 60 per cent. of the theoretical yield of formaldehyde and methyl alcohol (1 : 2). The *Bad. Anilin- und Soda-Fabrik, Ludwigshafen* (German Patent, 185,932), pass a mixture of formic acid vapours and hydrogen gas over heated metals, such as iron, nickel, tin, lead, etc., or other catalytic agents.

*Goldschmidt* (German Patent, 183,856) passes the vapour of formic acid over moderately heated tin oxide ( $180^{\circ}\text{C}$ .). Tin formate is formed, which, at the temperature employed, breaks up into formaldehyde,  $\text{CO}_2$ , and tin oxide. Most of the formaldehyde at once condenses to **paraformaldehyde** which is easily obtained pure by sublimation, and the method, therefore, is a convenient one for the manufacture of **paraformaldehyde**. A considerable amount of **methyl formate**,  $\text{H.COOCH}_3$ , is simultaneously produced, and is used either as such, or split by hydrolysis into methyl alcohol and formic acid.

**Paraformaldehyde** is usually made by evaporating an aqueous solution of formaldehyde. It then remains as a white amorphous mass,  $(\text{HCHO})_n$ , which on drying passes into **trioxymethylene**,  $(\text{HCHO})_3$ . This body volatilises between  $180^{\circ}$ - $200^{\circ}\text{C}$ ., turning into formaldehyde again. It is sold in the form of pastilles.

**Uses.**—Formaldehyde is used in very large quantities as a disinfectant, especially of rooms. It is used as a preservative for crude, raw products in tanneries, knackers' yards, soap works, etc. It is often added to gums, glues, or starch solutions for a similar purpose. It is also used extensively in many industries, such as in leather making, in the indiarubber goods industry, in photography, etc. etc. It forms an insoluble compound with gelatine, and condenses with phenols, etc., to form phenol-formaldehyde plastics (see under **Plastics**), etc. It is also used by gardeners to protect plants from parasites.

The **Formaline** of commerce contains about 35 per cent. of formaldehyde, and has a sp. gr. 1.079-1.081, as is shown by the following table:—



## SPECIFIC GRAVITY OF FORMALDEHYDE SOLUTION (FORMALINE) AT 18.5° (Züttke)

Per Cent. HCHO.	Specific Gravity.	Per Cent. HCHO.	Specific Gravity.	Per Cent. HCHO.	Specific Gravity.	Per Cent. HCHO.	Specific Gravity.
1	1.002	11	1.027	21	1.052	31	1.076
2	1.004	12	1.029	22	1.055	32	1.077
3	1.007	13	1.031	23	1.058	33	1.078
4	1.008	14	1.033	24	1.061	34	1.079
5	1.015	15	1.036	25	1.064	35	1.081
6	1.017	16	1.039	26	1.067	36	1.082
7	1.019	17	1.041	27	1.069	37	1.083
8	1.020	18	1.043	28	1.071	38	1.085
9	1.023	19	1.045	29	1.073	39	1.086
10	1.025	20	1.049	30	1.075	40	1.087

**Statistics.**—The United States imported in 1910, 34,000 lbs. of formic acid (value \$9,000). For modern statistics see Appendix III.

Acetaldehyde,  $\text{CH}_3\text{CHO}$ ,

Is largely manufactured from the first runnings of rectifying stills in the manufacture of spirits. It is formed by the oxidation of alcohol; when crude alcohol is purified by treating with animal charcoal a considerable amount of acetaldehyde is produced. Acetaldehyde is sometimes manufactured by oxidising alcohol (3 parts) with  $\text{K}_2\text{Cr}_2\text{O}_7$  (3 parts) and 16 parts of  $\text{H}_2\text{SO}_4$  solution (25 per cent.). The acetaldehyde (B.P. 21° C.) distils from the mixture, and is absorbed by dry ether; then dry  $\text{NH}_3$  gas is led into the ethereal solution and the aldehyde separated as aldehyde ammonia. This, when distilled with dil.  $\text{H}_2\text{SO}_4$ , yields acetaldehyde, which is dehydrated over  $\text{CaCl}_2$ .

**Properties.**—Colourless, mobile liquid with a peculiar odour. B.P. 20.8° C.; M.P. -120° C.;  $D_4$ , 0.8009. Mixes in all proportions with water and alcohol.

**Uses.**—For making quinaldine, quinoline yellow, hydrazine, etc.

**Paraldehyde**,  $(\text{CH}_3\text{CHO})_3$ , a liquid polymer of acetaldehyde (obtained by treating acetaldehyde with small quantities of acids or salts—such as  $\text{HCl}$ ,  $\text{H}_2\text{SO}_4$ ,  $\text{ZnCl}_2$ , etc.—at ordinary temperatures), finds some application in medicine as a sleep inducer.

## III. ALCOHOLS

For the manufacture of **Methyl Alcohol**, see under **Wood Distillation**. For **Ethyl Alcohol** see under **Spirits**. For **Butyl** and **Amyl Alcohol** see under **Fusel Oils**, p. 314.

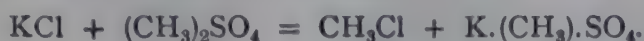
## IV. HALOGEN DERIVATIVES

Methyl Chloride,  $\text{CH}_3\text{Cl}$ ,

Is obtained from the residues of beetroot molasses, p. 163, by distillation with lime. The aqueous distillate is neutralised with  $\text{HCl}$  and the methyl alcohol distilled off. The residual liquor is then concentrated,  $\text{NH}_4\text{Cl}$  crystallises out, while the mother liquors contain **trimethylamine chloride**,  $\text{N}(\text{CH}_3)_3\text{HCl}$ . These are evaporated to dryness and heated to 350° C. with  $\text{HCl}$  under pressure, when methyl chloride is formed:  $(\text{CH}_3)_3\text{N.HCl} + 3\text{HCl} = 3\text{CH}_3\text{Cl} + \text{NH}_4\text{Cl}$ . (Vincent, see *Ding. Pol. J.*, 230, 272; "Jahresber.," 1878, 1135.) Weinland & Schmid ("Ber." (1905), 38,



2327) show that dimethylsulphate readily yields  $\text{CH}_3\text{Cl}$  when allowed to flow into a warm very concentrated solution of  $\text{KCl}$ :—



To purify the gaseous  $\text{CH}_3\text{Cl}$ , it is washed with water, dried with concentrated  $\text{H}_2\text{SO}_4$ , and condensed to a liquid in strong steel cylinders.

**Properties.**—*Gas*; sweet odour; B.P.  $-24^\circ \text{C}$ .; M.P.  $-103^\circ \text{C}$ . Used in making aniline colours; also for producing cold.

### Ethyl Chloride, $\text{C}_2\text{H}_5\text{Cl}$ , and Ethyl Bromide, $\text{C}_2\text{H}_5\text{Br}$ ,

Are manufactured by mixing concentrated  $\text{H}_2\text{SO}_4$  (2 parts) with 96 per cent. alcohol (1 part), and, after standing, diluting with water ( $\frac{1}{2}$  part), adding  $\text{KCl}$  or  $\text{KBr}$  (1 part) and distilling. Ethyl chloride, B.P.  $12.5^\circ \text{C}$ ., is used as a local anæsthetic; it produces great cold when it evaporates. **Ethyl Bromide**, B.P.  $38^\circ \text{C}$ . This preparation is used as an anæsthetic. Crude commercial ethyl bromide is now made by allowing 6 parts of bromine to slowly flow into a mixture of 1 part red phosphorus and alcohol, shaking and cooling continually during the operation. It always contains traces of poisonous phosphorus compounds.

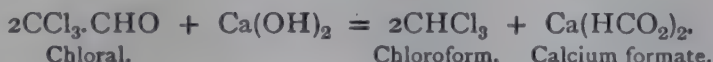
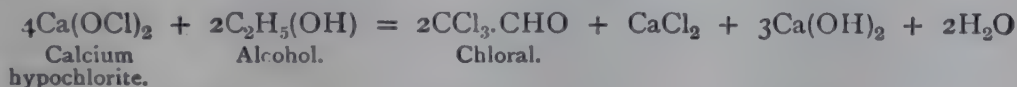
109 gals. (value £534) of ethyl chloride and 77 gals. (value, £13) of ethyl bromide were imported into England in 1910. The duty on ethyl chloride is £1. 1s. 10d. per gallon, and on ethyl bromide 1s. 5d. the lb. See also **General Anæsthetics**.

The import into the United States was 5,800 lbs. (value \$4,900) in 1910. Duty 30 per cent. For modern statistics see Appendix III.

### Chloroform, $\text{CHCl}_3$

#### 1. Manufacture by Heating together Alcohol and Bleaching Powder.

—The action is complex, chloral (see under) being first formed, which decomposes in the presence of the calcium hydrate of the bleaching powder into chloroform and calcium formate. Aldehyde is simultaneously produced:—



300 kg. of 96 per cent. alcohol and 1,300 l. of water are placed in iron boilers 1.40 m. in height and 2 m. in diameter, provided with powerful stirring apparatus, a man-hole (for charging with bleaching powder), inlet tubes for steam and water, and, in the cover, a tube for leading away the evolved vapours into the condenser, which consists of a copper spiral immersed in cooling water. Now 400 kg. of bleaching powder, containing 20-22 per cent. available chlorine, is gradually added while the stirring apparatus is in rapid action, the man-hole closed, and the vessel heated by steam until the temperature reaches  $40^\circ \text{C}$ . The steam is then shut off, but the temperature continues to increase. When it reaches  $45^\circ \text{C}$ . the stirring is stopped. At  $60^\circ \text{C}$ . the action reaches a maximum, and any further temperature increase is prevented by running cold water over the generator. A glass tube let into the leading tube as it comes from the condenser to the collector allows the operator to see at this stage a fine rain of chloroform, water, and alcohol blowing through the outlet tube into the vessel for collecting the distillate.

This vigorous action lasts for about a minute, and then chloroform begins to distil over in a rapid stream, and is received in tinned iron vessels. The issuing air, saturated with  $\text{CHCl}_3$  vapour, is caused to bubble through water, and is thus freed from chloroform. When about 30 kg. of  $\text{CHCl}_3$  have distilled over, the stirring apparatus is again set in action until the distillate ceases to separate out into two layers, the heavy chloroform being underneath. At this stage the receiver is changed, and the distillation continued until the distillate ceases to give a turbidity with water, when it contains no more chloroform. The receiver is again changed until the distillate acquires the density  $3^\circ \text{Trallés}$ . The operation is then stopped, the lime being run off through a valve placed in the bottom of the generator. **Yield, 31-31.5 kg. Chloroform.** The dilute alcohol distilled over is mixed with the requisite amount of alcohol to make it of the same composition as the original alcoholic charge, and is used again for repeating the operation with a new charge of bleaching powder.

The chloroform contains alcohol and ether; it is purified by rectification. When it is to be used as an anæsthetic, the commercial chloroform is washed in



succession with distilled water, with dilute (2.5 per cent.)  $\text{H}_2\text{SO}_4$  (for two to three days); with a 3 per cent. solution of  $\text{NaOH}$ , and finally again with distilled water; it is dried over fused  $\text{CaCl}_2$ , a small amount of poppy-seed oil added, the whole distilled, and the distillate, which should boil at  $61^\circ \text{C}$ ., is mixed with 2 per cent. of pure absolute alcohol. This is done because  $\text{CHCl}_3$ , especially under the action of light, undergoes a slow spontaneous decomposition, with formation of chlorine and the poisonous phosgene gas,  $\text{COCl}_2$  (to whose influence many fatal accidents have been traced); the addition of a small percentage of alcohol increases the stability of chloroform. The chloroform is kept in stout bottles with ground glass stoppers, rendered air-tight with chromatised gelatine. Pictet purifies  $\text{CHCl}_3$  by freezing at  $-70^\circ \text{C}$ . to  $-100^\circ \text{C}$ ., and centrifugalling the crystalline mass from the impure liquid portions.

**2. Manufacture from Acetone and Bleaching Powder.**—The process is much the same as with alcohol, but the yield is better, 100 kg. acetone giving 175 kg.  $\text{CHCl}_3$ . 270 parts of bleaching powder are mixed with 800 parts of water, and gradually added to 22 parts of acetone and 70 parts of water.  $\text{CHCl}_3$  is generated, with the evolution of heat, and distils off. Towards the end of the reaction, a gentle external heating is applied.

**3. Manufacture by Besson's Continuous Process.**—By this process (German Patent, 129,237) chloroform is obtained from alcohol in almost theoretical quantity, and in an extremely pure state; moreover, the process has the great advantage of being a continuous one. Alcohol, as free from water as possible, is chlorinated by dry chlorine gas until the chlorination product attains a density of  $25^\circ$ – $35^\circ \text{Bé}$ ., or even more, whereby chloral hydrate or a similar body is produced. The chlorinated alcohol is now treated with milk of lime or other caustic alkali with gentle heating, when pure chloroform is evolved, probably according to the equation:— $\text{CCl}_3\text{CO.H} + \text{NaOH} = \text{CHCl}_3 + \text{HCOONa}$ .

Fig. 166 illustrates Besson's apparatus:—

A stream of alcohol slowly runs from *c* into the vessel *a*, flowing in succession over a number of shallow trays *b*, placed one below the other as seen in the figure. A stream of dry chlorine gas enters by *d*, meets the stream of flowing alcohol, saturates it, and escapes through *h*. The chlorinated alcohol collects in the holder *e* and thence pours into the funnel-like base of the chlorinator *a*. Fragments from the vessel—*e.g.*, lead chloride, etc., produced by the destructive action of chlorine on the leaden walls—can be run off into *g*. *k* are steam coils for producing the necessary degree of warmth for the chlorination to take place most readily. The chlorinated alcohol, together with any vapours (which are condensed in *j*) flow through a cooler *j* up the tube *o* into the vessel *m*, which is charged with bleaching powder. The mixture is slowly forced thence, by means of a screw worm, through *q* into the large chamber *l*, also containing a screw worm *r* and steam heating coils *s*. A stream of milk of lime is slowly forced into the apparatus from *n*, and the worm *r* slowly mixes and forces the mass along the chamber *l* and out through *t*. The chloroform vapours escape through tubes *w* in the cover of the apparatus, through *x* into the condenser *p*, or direct into a rectifying apparatus.

It is stated that 100 parts of alcohol yield from 95–105 parts of pure chloroform.

4. Among other methods of manufacturing chloroform may be mentioned: (*a*) the electrolysis of an alcoholic solution of  $\text{CuCl}_2$  (not a commercial success up to the present); (*b*) by distilling pure chloral with  $\text{NaOH}$ :— $\text{CCl}_3\text{CHO} + \text{NaOH} = \text{CHCl}_3 + \text{HCOONa}$  yields a very pure product; (*c*) when salicylide,  $(\text{C}_6\text{H}_4\text{CO})_2$ —an anhydride produced by warming salicylic acid with phosphorus oxychloride—is dissolved in crude chloroform, it crystallises out with two molecules of  $\text{CHCl}_3$ . On distilling the crystals on the water bath perfectly pure  $\text{CHCl}_3$  distils over, leaving behind the salicylide to be used again for another operation. (Anschütz.)

**Properties.**—Colourless liquid, with sweetish pleasant taste and smell. B.P.  $61.5^\circ \text{C}$ .;  $D_{15}$ , 1.5008. When used as an anæsthetic contains 2 per cent. alcohol.

For further information see under **Anæsthetics**, p. 602.

**Uses.**—Largely in medicine as an anæsthetic. Technically it is used as a solvent, especially for rubber, gutta-percha, etc. Also as a cleansing agent.



**Statistics.**—*German exports* of  $\text{CHCl}_3$ : 1908, 1,300 dz.: 1909, 1,480 dz. (1 dz. = 100 kilos =  $\frac{1}{10}$  ton.)

The English import of chloroform was 1,774 lbs. (value £299), and the export 1,531 lbs. (value £158) in 1910. The duty on chloroform is 4s. 4d. the lb.

The United States imported in 1910, 967 lbs. of chloroform (value \$1,400). The American duty is 10 cents the lb.

For modern statistics see Appendix III.

### Chloral, $\text{CCl}_3\text{CHO}$ ; Chloral Hydrate, $\text{CCl}_3\text{CH}(\text{OH})_2$

**Manufacture.**—A slow stream of dry chlorine gas is led into 96 per cent. alcohol, at first in the cold, but afterwards with gentle warming ( $60^\circ \text{C.}$ ), until  $\text{HCl}$  ceases to be evolved. 7 kg. alcohol require two weeks for complete chlorination. The action is complex, but finally chloral,  $\text{CCl}_3\text{CHO}$ , is formed as a heavy oil. It is purified by treating with concentrated  $\text{H}_2\text{SO}_4$ , then distilled from  $\text{H}_2\text{SO}_4$ , dried and rectified, the part passing over between  $94^\circ$ – $95^\circ \text{C.}$  being pure chloral. It forms an oily liquid, with a penetrating smell.  $D_4$ , 1.541; B.P.  $97^\circ \text{C.}$  On keeping it passes into solid **metachloral**.

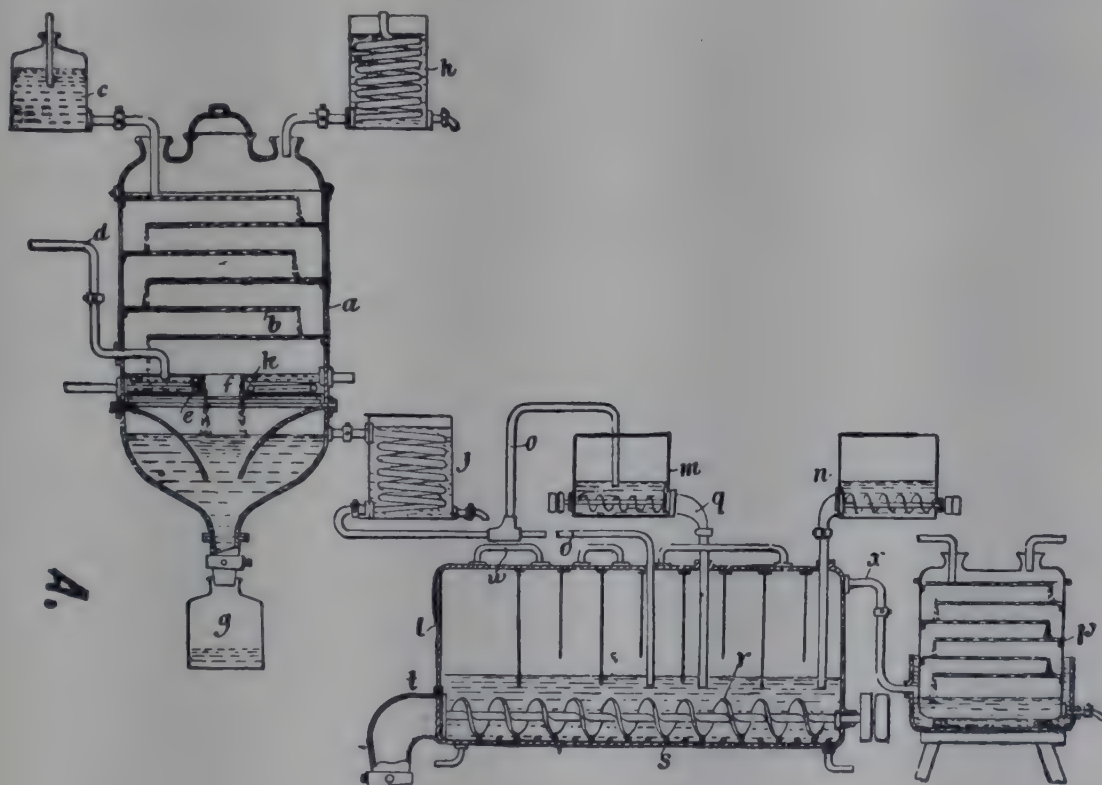


FIG. 166.—Besson's Process for the Manufacture of Chloroform.

To produce **chloral hydrate** 100 parts of chloral are mixed with 12.25 parts of water, when combination ensues and a mass of large monoclinic crystals are produced. Chloral hydrate heated with alkalis yields pure  $\text{CHCl}_3$ . Heated to  $57^\circ \text{C.}$  it decomposes to chloral and water. It is used in medicine as a sleep producer, but is now being replaced by other more efficient drugs. (See **Hypnotics**, p. 608).

The English duty on chloral hydrate is 1s. 9d. the lb. The English import of chloral hydrate was 20,000 lbs. (value £3,400) in 1906, and 28,800 lbs. (value £2,760) in 1910.

The American duty on chloral hydrate is 55 cents. per lb. (1910). The United States in 1910 imported 171,000 lbs. (value \$152,000).

### Polychlorals, $(\text{CCl}_3\text{CHO})_x$ (see **Hypnotics**, p. 608),

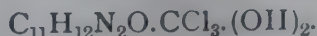
Are produced by treating chloral with amines (such as pyridine) or chloral hydrate with concentrated  $\text{H}_2\text{SO}_4$  (see German Patents, 165,984, 170,534). They are soluble in water and are used as anæsthetics and hypnotics.

**Dormiol,**

A liquid soporific, is chloralamylalcoholate,  $\text{CCl}_3\cdot\text{CH}(\text{OH})\cdot\text{OC}_5\text{H}_{11}$ , produced from chloral and amyl alcohol.

**Hypnal,**

Similarly produced from chloral hydrate and antiypyrine, has the formula:—

**Dimethylethylcarbinolchloral,  $\text{Cl}_3\cdot\text{CH}(\text{OH})\cdot\text{O}\cdot\text{C}(\text{CH}_3)_2\cdot\text{C}_2\text{H}_5$ ,**

Is produced by warming to  $60^\circ$  a mixture of chloral hydrate and amylene hydrate,  $\text{C}_2\text{H}_5\cdot\text{C}(\text{CH}_3)_2\cdot\text{OH}$ .

**Chloralformamide,  $\text{CCl}_3\cdot\text{CH}(\text{OH})\cdot\text{NH}\cdot\text{CHO}$ ,**

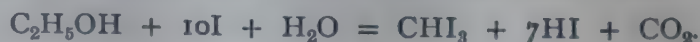
Is similarly produced from chloral and formamide.

**Chloralacetonechloroform,  $\text{CCl}_3\cdot\text{CH}(\text{OH})\cdot\text{O}\cdot\text{C}(\text{CCl}_3)\cdot(\text{CH}_3)_2$** 

Is similarly produced from acetone chloroform and chloral hydrate (German Patent, 151,188). A valuable local anæsthetic and hypnotic.

**Iodoform,  $\text{CHI}_3$** 

Iodoform was formerly exclusively made by warming alcohol or acetone with iodine and caustic soda or alkaline carbonate; more recently Dr Marius Otto (German Patent, 109,013) made it by simply leading ozone into a mixture of potassium iodide (55), sodium carbonate (10), alcohol (300), water (100), warmed to  $50^\circ$  C. By far the greater part, however, is now made electrolytically, a very pure product being thus obtained (Elbs and Herz, *Zeit. f. Elektroch.*, 1897, 4, 113; Förster and Mewes, *loc. cit.* (1897), 4, 268; *J. pr. ch.*, 1897, 56, 353). A solution of sodium carbonate (5), potassium iodide (10), alcohol (20), water (100), is subjected to electrolysis at  $60^\circ$  C. by a current density (anodic) of 1 ampère per 1 sq. dm., using a porous cell as diaphragm around the anode; the cathode may be surrounded with a cell of parchment paper and a stream of  $\text{CO}_2$  passed through the liquid. The nascent oxygen set free at the anode liberates the iodine from the KI, which then combines with the alcohol and water to produce iodoform:—



The iodoform is hourly removed and the solution made up to its original strength by the addition of  $\text{Na}_2\text{CO}_3$ , KI, and alcohol. Iodoform is a somewhat volatile yellow solid, with a characteristic odour, largely used as an antiseptic for wounds.

For modern statistics see Appendix III.

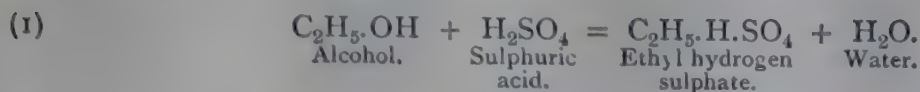
## V.—THE ETHERS

**Ether, Sulphuric Ether,  $(\text{C}_2\text{H}_5)_2\text{O}$ ,**

Is prepared on a very large scale by heating to boiling ( $140^\circ$ – $145^\circ$  C.) in a large lead-lined vessel A a mixture of 9 parts concentrated  $\text{H}_2\text{SO}_4$  and 5 parts 96 per cent. alcohol, while simultaneously a constant flow of alcohol into the boiling liquid takes place from a tank B through a leaden pipe dipping into the liquid. The inflowing alcohol is added at such a rate that the volume of the mixture remains unchanged and the continuous ebullition proceeds smoothly without breaks.



The following action takes place :—



Side actions simultaneously take place, producing sulphonic acids and esters (e.g.,  $\text{HO}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{SO}_2\cdot\text{O}\cdot\text{C}_2\text{H}_5$ ) which are found in commercial ether (see *Prunier, Comp. Rend.*, 1897, **124**, 1028, 1239). The sulphuric acid, although continually regenerated, gradually becomes diluted with water and is partially destroyed by the side actions, so that after a time its efficiency ceases. 600 kg. of  $\text{H}_2\text{SO}_4$  (sp. gr. 1.840) suffice to convert 40,000 kg. of 96 per cent. alcohol into ether in the course of a six weeks' continuous operation.

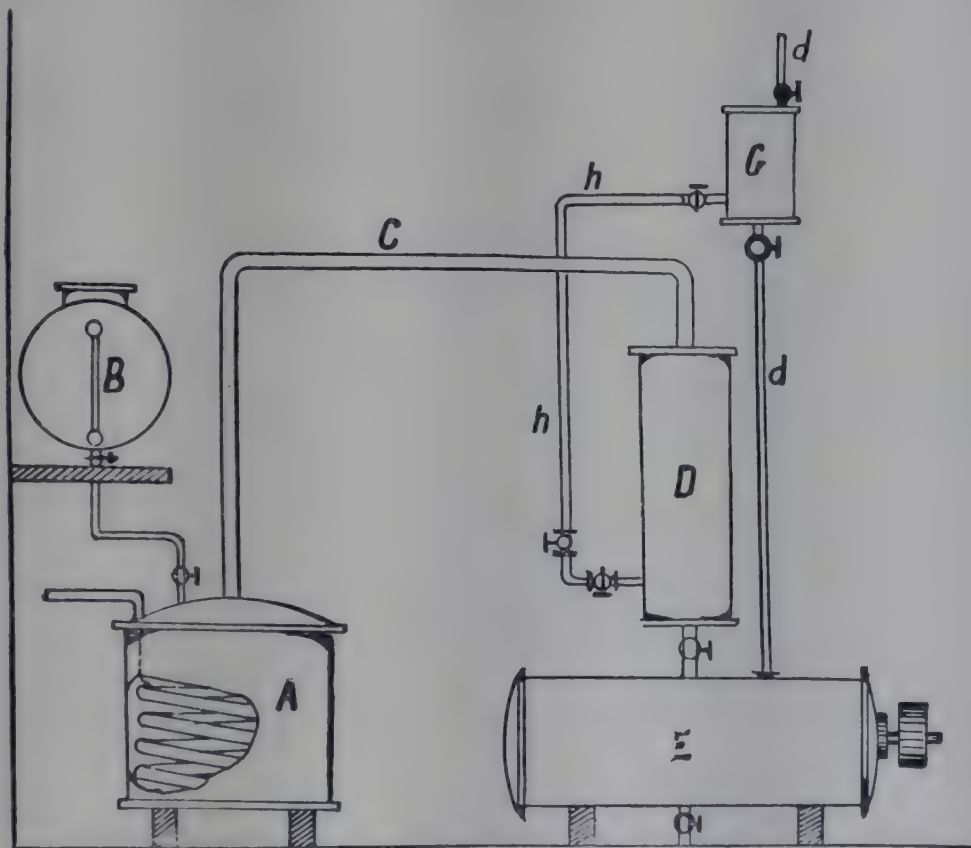
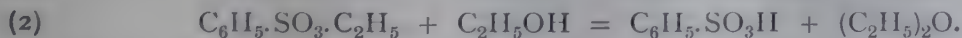


FIG. 167.—Manufacture of Ether.

Krafft and Roos (German Patent, 69,115) in their process replace the sulphuric acid by **benzene sulphonic acid** and thus avoid the formation of volatile sulphonic acids :—



A recent proposal by Schröter and Sondag ("Ber.," 1908, **41**, 1921) to replace sulphuric acid by **methiononic acid**,  $\text{CH}_2(\text{SO}_3\text{H})_2$ , promises to become important. If a mixture of alcohol and methiononic acid is heated to  $140^\circ$  and a stream of alcohol allowed to flow into the liquid as described above, ether and water continually distil over while the methiononic acid undergoes no change. The method is especially valuable for producing ethers of high molecular weights. For example di-iso-amylether is produced by merely heating amyl alcohol with one-tenth of its weight of methiononic acid.

The ether distilling away from A passes by means of the tube c into the condenser D and runs into the tank E, where it is agitated by stirrers with milk of lime or sodium carbonate solution in order to remove any acid carried off. Permanent gases produced in the reaction (e.g., ethylene) escape through the tube dd into the air, the condenser G returning any ether vapour to D and E by means of the tube hh.

The crude ether is now drawn off and separated from alcohol by rectifying in an ordinary still. It is then carefully rectified in columnar stills.

**Methods of Purifying Commercial Ether.**—The usual process for purifying ether consists in shaking with water (which removes alcohol) and distilling. Dr H. Timpe (German Patent, 124,230) obtains a pure water and alcohol free ether without distillation by shaking it with aqueous  $\text{H}_2\text{SO}_4$  of 30-50 per cent. concentration, which absorbs both water and alcohol. Most of the water taken up at  $18^\circ \text{C}$ . may be frozen out by cooling the ether in a freezing mixture. The purest sorts of ether are obtained by treating with metallic sodium which destroys all water and alcohol, distilling, and keeping over sodium.

The laboratory method of purifying commercial ether consists in washing twice with water, keeping two days over calcium chloride, treating with sodium wire for two to three days until hydrogen ceases to be evolved, and distilling over phosphorus pentoxide. It should be kept in stout bottles with stoppers waxed in, or else over sodium wire in a bottle provided with a calcium chloride tube.

**Properties.**—B.P.  $35^\circ \text{C}$ . at 760 mm.; M.P.  $-113^\circ \text{C}$ .;  $D_0$ , 0.736;  $D_{15}$ , 0.720. 100 parts ether dissolve 3 parts water; 100 parts water dissolve 10 parts ether. Vapour very inflammable and forms an explosive mixture with air. An excellent solvent for organic compounds.

**Uses.**—Used as a solvent and extracting agent, especially in the manufacture of celluloid, etc. etc. Also used as an anæsthetic for minor operations, since its vapour produces first intoxication and then unconsciousness.

The United States in 1910 imported 337 lbs. of ether (value \$66). The duty is 8 cents per lb. For modern statistics see Appendix III.

### Methyl Ether, $\text{CH}_3\text{O.CH}_3$ ,

Is prepared from methyl alcohol and sulphuric acid in exactly the same way that ordinary ether is prepared from ethyl alcohol and sulphuric acid. Colourless gas, with ethereal odour, condensing at  $-21^\circ \text{C}$ . to a colourless liquid. 1 vol.  $\text{H}_2\text{O}$  dissolves 37 vols. of the gas, 1 vol.  $\text{H}_2\text{SO}_4$  over 600. Used instead of ammonia in ice-producing machines.

## VI. THE ESTERS (ALSO CALLED ETHERS), INCLUDING FRUIT ESSENCES.

These are produced by heating together a mixture of an alcohol and an organic acid, usually in the presence of some dehydrating agent, such as sulphuric acid dry  $\text{HCl}$  gas, etc. The mixture is then fractionally distilled. Many esters are conveniently prepared by dissolving the organic acid in the alcohol, saturating the mixture with dry  $\text{HCl}$  gas, separating the ester as an oil by adding water, drying, and distilling.

### Ethyl Formate, $\text{H.CO.O.C}_2\text{H}_5$ ,

Is prepared by distilling a mixture of alcohol, oxalic acid (dehydrated), and glycerol. The oxalic acid splits up into formic acid and  $\text{CO}_2$ . The nascent formic acid immediately combines with the alcohol, giving the ester. Volatile liquid, B.P.  $54.5^\circ \text{C}$ .; used in the preparation of artificial rum and arrak.

### Ethyl Acetate (Acetic Ether), $\text{CH}_3\text{CO.O.C}_2\text{H}_5$ ,

Is prepared on a large scale by boiling together a mixture of alcohol, acetic acid, and  $\text{H}_2\text{SO}_4$ , usually in a steam-heated copper still, provided with a rectifying column. The distillate flows into a vessel provided with stirring apparatus, and is there



washed with alkali to remove  $\text{H}_2\text{SO}_4$ , then with water, dried over  $\text{CaCl}_2$ , and rectified over calcined magnesia. It is less frequently prepared by heating dehydrated sodium acetate with concentrated  $\text{H}_2\text{SO}_4$  and alcohol. Ethyl acetate may be freed from alcohol by heating for thirty minutes with a reflux condenser over  $\text{P}_2\text{O}_5$ , and then distilling.

**Properties and Uses.**—Pleasant smelling liquid, B.P.  $77.5^\circ \text{C}$ .; used as a solvent in making smokeless powder, and in other industries as well. Much used as a synthetic agent in chemistry, for example in the manufacture of **anti-pyrine**. Also used for perfuming fruit juices, spirits, etc., and in medicine.

#### Glycerol Acetate, Acetine, $\text{C}_3\text{H}_5(\text{O}.\text{C}_2\text{H}_3\text{O})_3$ ,

Is obtained by heating together glycerol and glacial acetic acid. Used as a solvent (possessing certain advantages over alcohol, etc.) for **induline** and other colouring matters employed by the calico printer as a steam colour; also employed as an adulterant of peppermint oil and other ethereal oils. Said to be employed for gelatinising and lowering the freezing point of nitroglycerine (see p. 624).

#### Ethyl Butyrate (Butyric Ether), $\text{CH}_3(\text{CH}_2)_2\text{COOC}_2\text{H}_5$

The ethyl butyrate of commerce is really a mixture of the ethyl esters of normal **butyric acid**,  $\text{CH}_3(\text{CH}_2)_2\text{COOH}$ , and of other similar acids. It is obtained: (1) by distilling rectified butyric acid with alcohol and sulphuric acid; (2) by saponifying butter with caustic soda and distilling the resulting soap with alcohol and  $\text{H}_2\text{SO}_4$ ; (3) the pod of the carob bean, *Silqua dulcis*, is chopped up, mixed with chalk mud, and allowed to ferment. The pod contains 2 per cent. **iso-butyric acid**,  $(\text{CH}_3)_2\text{CH}.\text{COOH}$ , and 40 per cent. sugar; this ferments to *n*-butyric acid, and, after some weeks, the calcium butyrate is isolated and distilled with alcohol and sulphuric acid, when the ester is produced.

The substance is used for flavouring purposes; B.P.  $110^\circ\text{--}121^\circ \text{C}$ .

#### Amyl Butyrate, $\text{CH}_3(\text{CH}_2)_2\text{COOC}_5\text{H}_{11}$ ,

Is obtained in a similar manner to ethyl butyrate, replacing, however, the alcohol by fusel oil amyl alcohol. Used in making "apricot essence."

#### Amyl Acetate, $\text{CH}_3\text{CO}.\text{O}.\text{C}_5\text{H}_{11}$ ,

Is obtained from amyl alcohol and acetic acid by heating in the presence of  $\text{H}_2\text{SO}_4$ , distilling or by saturating the mixture with dry  $\text{HCl}$  gas, adding water, and separating the oil. Pure amyl acetate boils at  $138^\circ \text{C}$ . It has a pleasant "pear-like" odour and, when mixed with ethyl acetate and alcohol (1 : 10), is sold as "**Pear Oil**" for flavouring confectionery, sweets, etc. Pure amyl acetate is used as a standard oil in photometry (Hefner Lamp). It is also used as a solvent for many technical purposes. (See pp. 49, 298, 312.)

*Butyl Acetate*, produced from butyl alcohol and acetic acid, has similar solvent powers to amyl acetate (see p. 314).

#### Amyl-iso-valerate, $\text{C}_4\text{H}_9\text{CO}.\text{OC}_5\text{H}_{11}$ ,

Is obtained from amyl alcohol from fusel oil by oxidising it with potassium dichromate and  $\text{H}_2\text{SO}_4$ . Five parts of powdered potassium dichromate are placed in



a vessel provided with a reflux condenser. 4 parts of water are added, and then a mixture of 1 part of the amyl alcohol, B.P.  $129^{\circ}$ - $131^{\circ}$ , and 4 parts of concentrated  $\text{H}_2\text{SO}_4$  allowed to run slowly in. A vigorous action ensues, owing to the formation first of **iso-valeric acid**, which then unites with amyl alcohol to produce amyl-iso-valerate, thus:  $3\text{C}_5\text{H}_{12}\text{O} + 2\text{O}_2 = (\text{C}_5\text{H}_{11})\cdot\text{O}\cdot(\text{C}_5\text{H}_9\text{O}) + \text{C}_5\text{H}_{10}\text{O}_2 + 3\text{H}_2\text{O}$ . When the reaction slackens the liquid is boiled until iso-amyl aldehyde (known by its suffocating smell) ceases to escape through the reflux condenser. The liquid is then distilled, the distillate neutralised with sodium carbonate, when the amyl-iso-valerate separates as an oil. This is run off, dried, and rectified. Another method of producing amyl-iso-valerate is to distil a mixture of 12 parts dehydrated sodium valerate with 8 parts of amyl alcohol and 12 parts concentrated  $\text{H}_2\text{SO}_4$ .

**Properties.**—Oily liquid, B.P.  $188^{\circ}$ . Has a pleasant smell of apples, and consequently is sold under the name "apple-oil" for flavouring sweets, liquors, etc.

### Amyl Capronate, $\text{CH}_3\cdot(\text{CH}_2)_8\cdot\text{COOC}_5\text{H}_{11}$ ,

Is the main constituent of cocoa-nut oil essence or cognac essence, which contains as well ethyl esters of capronic, caprylic, lauric, myristic, and palmitic acids. It is obtained from the volatile acids of cocoa-nut oil (formed by saponifying the oil, decomposing the resulting soap by  $\text{H}_2\text{SO}_4$ , and steam distilling). The volatile acids are dried, mixed with amyl alcohol, saturated with dry  $\text{HCl}$  gas, and heated. ( $\text{H}_2\text{SO}_4$  may be used instead.) After twenty-four hours the ester is separated as an oil by adding water, agitated with  $\text{Na}_2\text{CO}_3$  solution, washed with water and rectified.

The substance is used for flavouring **artificial cognacs**. It is very similar to **wine oil**, which is obtained by distilling wine (see p. 251).

### Methyl Benzoate, $\text{C}_6\text{H}_5\cdot\text{CO}\cdot\text{O}\cdot\text{CH}_3$ ,

Is obtained by distilling benzoic acid and methyl alcohol with  $\text{H}_2\text{SO}_4$ . Used in perfumery as **Niobe Oil**. B.P.  $199.2^{\circ}$  C. (746 mm.).

### Ethyl Benzoate, $\text{C}_6\text{H}_5\text{CO}\cdot\text{OC}_2\text{H}_5$ ,

Prepared by action of dry  $\text{HCl}$  gas on benzoic acid dissolved in alcohol. Separates as an oil on adding water. B.P.  $213^{\circ}$ . Used for manufacturing essences and perfumes. Also in synthetic chemistry, for introducing the benzoyl group into certain synthetic drugs, especially local anæsthetics.

### Methyl Salicylate, $\text{C}_6\text{H}_4(\text{OH})\cdot\text{COO}\cdot\text{CH}_3$ ,

Is obtained in a similar manner by distilling methyl alcohol, salicylic acid, and  $\text{H}_2\text{SO}_4$ . Occurs naturally in oil of wintergreen (from *Gaultheria procumbens*). Used in perfumery and in medicine.

### Methoxymethylsalicylate, $\text{C}_6\text{H}_4(\text{OH})\cdot\text{COO}\cdot\text{CH}_2\cdot\text{OCH}_3$ ,

Used in medicine under the name "Mesotan." Manufactured by the Elberfelder Farbenfabriken (German Patent, 137,585) by heating monochlormethyl ether,  $\text{CH}_2\text{Cl}\cdot\text{O}\cdot\text{CH}_3$  (prepared by passing  $\text{HCl}$  gas into a mixture of formaldehyde and methyl alcohol), dissolved in benzene, to  $40^{\circ}$  C. (not over) with sodium salicylate. The following action takes place:—



The product is washed with  $\text{H}_2\text{O}$ , the benzene distilled off, and the oil distilled *in vacuo*.

### Ethyl Nitrite, $\text{C}_2\text{H}_5\cdot\text{NO}_2$ ,

Is obtained by mixing 3 parts crude 40 per cent.  $\text{HNO}_3$  with 12 parts alcohol (sp. gr. 0.834-0.830) and distilling on the water bath until red fumes appear,



neutralising the distillate with calcined magnesia, and pouring off from this after twenty-four hours; 3 parts of alcohol are added and then the whole is rectified.

The substance decomposes, becoming acid on standing, when it must again be neutralised with magnesia and rectified. Ethyl nitrite boils at  $+16^{\circ}\text{C.}$ ; the commercial "Ethyl Nitrite" is an alcoholic solution of the substance. Used in the manufacture of the cheaper kinds of **essences**; also in medicine.

### Amyl Nitrite, $\text{C}_5\text{H}_{11}\text{NO}_2$ ,

Is prepared by heating pure amyl alcohol from fusel oil (B.P.  $130^{\circ}\text{--}131^{\circ}\text{C.}$ ) to  $70^{\circ}\text{--}90^{\circ}\text{C.}$ , and then passing in nitrous fumes until the smell of the amyl alcohol becomes imperceptible. The product is as rapidly as possible neutralised with calcined magnesia (or dilute sodium carbonate solution), dried over  $\text{CaCl}_2$ , and distilled on a water bath of boiling brine. The fraction  $90^{\circ}\text{--}100^{\circ}\text{C.}$  is collected and redistilled, when the pure product, B.P.  $96^{\circ}\text{C.}$ , comes over.

Amyl nitrite is a pleasant smelling liquid used in the manufacture of certain mineral waters, scents, sweets, etc., in spite of the fact that the substance is poisonous, causing headache, giddiness, and other unpleasant symptoms. It is used in the synthetic dye industry for preparing nitroso- and diazo-compounds. Also used to a small extent in medicine.

We append here the constitution of some **commercial fruit essences** (also fruit **ethers**) composed of the above-mentioned esters.

**Apple Essence.**—Amyl isovalerate, 100; ethyl nitrite, 50; ethyl acetate, 50; acetaldehyde,  $7\frac{1}{2}$ ; alcohol, 793 parts.

**Pear Essence.**—Amyl acetate, 200; ethyl nitrite, 100; ethyl acetate, 50; alcohol, 645.

**Apricot Essence.**—Amyl butyrate, 190; benzaldehyde, 35; alcohol, 770.

**Strawberry Essence.**—Amyl formate, 9; butyric acid, 9; isovaleric acid, 18; acetic acid, 27; ethyl acetate, 13; essence of violets, 9; alcohol, 915.

**Cherry Essence.**—Amyl acetate, 15; benzaldehyde, 10; sweet oil of oranges, 1; cassia oil, 2; lemon oil, 2; oil of cloves, 2; amyl butyrate, 8.

**Peach Essence.**—Amyl isovalerate, 100; amyl butyrate, 100; amyl acetate, 20; benzaldehyde, 10; alcohol, 770.

See also **Synthetic Perfumes**, p. 136.

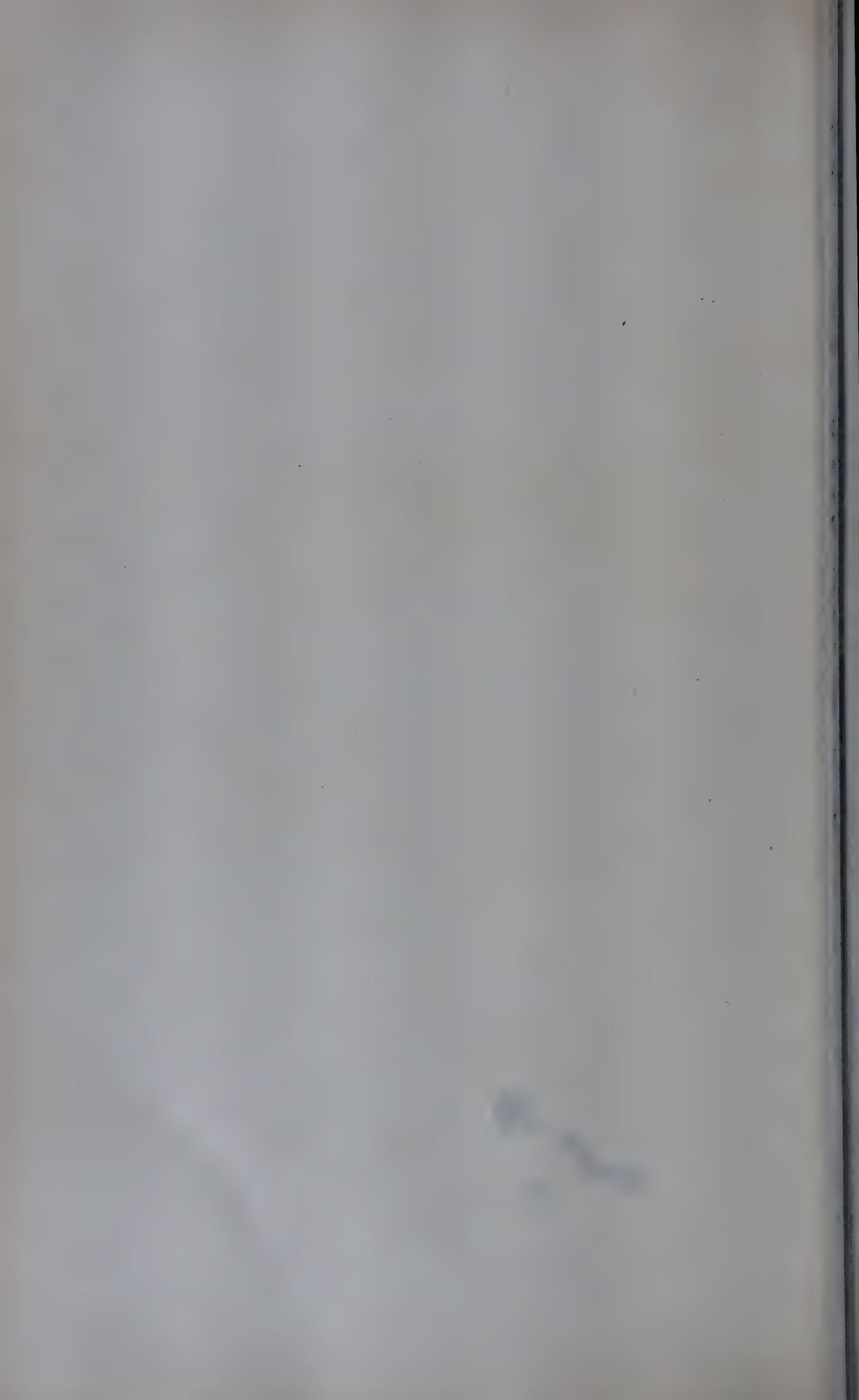




## SECTION XI

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### The Fuel Gas Industry





# THE FUEL GAS INDUSTRY

BY P. C. BISHOP, B.Sc., A.R.I.C., Assoc.M.Inst.Gas E.,  
AND R. A. JONES, B.Sc., A.R.I.C.

## LITERATURE

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THE Gas Industry originated in England with Murdoch in 1792. London streets were illuminated with gas in 1813, Paris in 1815, and Berlin in 1826. In its early years gas was used mainly as an illuminant, the light being derived from hot carbon particles in the unaerated flame. Its effectiveness as a source of light was greatly increased by the introduction of Auer’s incandescent mantle in 1885, with subsequent improvements in the design of the mantle and the materials used in its construction.

During the twentieth century other uses of gaseous fuels have increased to such an extent as to outweigh its use for lighting. Although gas lighting is still widely used in 1950, more importance is attached to other domestic applications such as water heating, space heating, and cooking, and to industrial applications in a wide field for power and for heating purposes. Industrial uses may vary from fish frying to furnace heating in steel works.

The fact that the incandescent mantle and other modern uses of gas all depend on the heating power or calorific value of the gas was recognised by the British Parliament in the Gas Regulation Act of 1920. This statute made its calorific value the standard by which the quality of gas is measured, the previous standard having been the illuminating power of an unaerated flame. The basis of charge adopted is the therm of 100,000 British Thermal Units. All major undertakings are required to supply gas of a declared calorific value, usually about 500 B.Th.U. per cubic foot.

The following statistics for the year 1947 refer to Great Britain:—

Coal carbonised: 22,500,000 tons.

Oil gasified: 168,600,000 gallons.

Gas made: 430,800 million cubic feet.

Gas bought from coke ovens for public distribution: 53,700 million cubic feet.

Total gas available for distribution: 484,500 million cubic feet.  
2,800 million therms.

It must be noted that these figures are affected to some extent by the coal shortage in that year, and that the oil gasified was greater by far than in any previous year.

The common fuel gases may be classified as follows:—

- (1) Coal gas, produced by the carbonisation or destructive distillation of coal in closed vessels.
- (2) Blue water gas, produced by passing steam through hot coke, the temperature of the coke being maintained by blowing air through the mass in the second stage of a cyclic process. Part of the coke is burnt in this stage and the waste gases rejected.

- (3) Carburetted water gas, produced by "cracking" oil vapour in blue water gas.
- (4) Producer gas, produced by passing air and steam together through hot coal or coke.
- (5) Natural gas from petroleum fields.
- (6) Petroleum refinery gas.
- (7) Sewage gas.
- (8) Acetylene.
- (9) Blast furnace gas.

## COAL GAS

**Carbonisation.**—The term "carbonisation" as used in the gas industry refers to the destructive distillation of bituminous coal in closed vessels. The following are the main products of the process:—

- (1) Gas.
- (2) Tar.
- (3) Aqueous liquor, condensed from the gas.
- (4) A solid residue of coke.

The composition and yield of all four products depends upon a number of factors which include the carbonising temperature, the design of the plant and the source of the coal carbonised.

Two processes are sharply distinguished in practice, as under:—

(1) Low temperature carbonisation, where the coke attains a final temperature of less than  $600^{\circ}\text{C}$ . This process is used in the production of smokeless solid fuels (*e.g.*, Coalite) and the residue is comparatively soft with a high content of combustible volatile matter. The gas from this process is comparatively small in quantity but of a very high calorific value.

(2) High temperature carbonisation, where the coke attains a final temperature of  $1,000^{\circ}\text{C}$ . or over. This process gives high gas yields, a heavier tar, and a hard coke with low volatile content.

The main object of high temperature carbonisation may be either the production of gas with coke as a by-product or the production of metallurgical coke with gas as a by-product. In some cases the same plant is used for both purposes. In the gasworks, coke is used as the source of heat for the process; usually it is fed to a producer and the resulting producer gas utilised for heating the retorts. In the cokeworks, on the other hand, coal gas is normally used for heating the ovens.

For gas manufacture there are three main types of plant:—

(1) **Horizontal Retorts.**—The horizontal retort is the oldest form of gas-making plant, and the modern horizontal installation is still for many purposes the most satisfactory type. It can give good yields of gas of a high calorific value. Control is simple and output flexible. The coke is usually satisfactory for domestic and industrial use, although not as hard as oven coke. The tar is largely benzenoid and up to three gallons of high-aromatic benzole can be extracted from the gas from every ton of coal. The high percentage of aromatic compounds in the products is accounted for by the high temperature to which the gas is subjected on its passage from the charge to the offtakes at either end of the retort. The temperature promotes the formation of aromatics from the primary products.

Fig. 168 shows a sectional view of a horizontal retort setting in a simplified form. The retorts themselves are of fireclay or silica and are either elliptical or  $\square$ -shaped. Dimensions vary with the size of the works, but 14 in. to 16 in. minor axis by 20 in. to 24 in. major axis are common. The length of the retort is usually about 20 ft. Retorts are fitted with an iron collar at each end, to which



are fastened the mouthpieces, doors, and gas offtakes. Heating is by means of producer gas made either in external producers or in internal ("built-in") producers. The sketch (Fig. 168) shows a built-in producer. The producer gas is burnt at refractory burners, the air for combustion (secondary air) often being preheated on its way to the burners. In this way a high combustion-chamber temperature is possible, and with a combustion-chamber temperature of  $1,350^{\circ}\text{C}$ . charges of coal are completely carbonised in some ten hours.

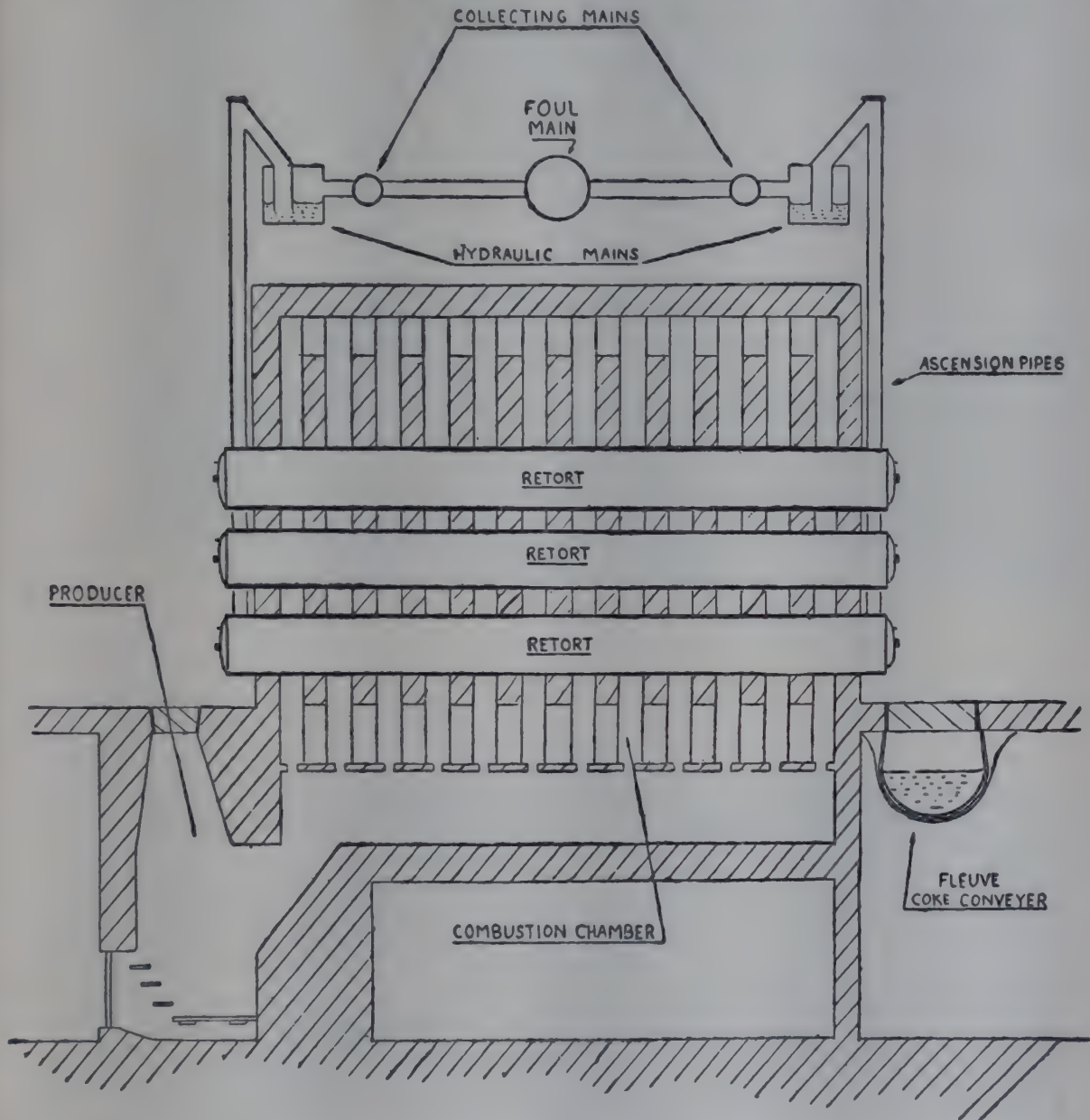


FIG. 168.—Section of Horizontal Retort Setting.

The cycle of operations is as follows: The hot empty retort is charged with coal crushed to less than two inches in size. A 20 ft.  $\times$  15 in.  $\times$  22 in. retort will take some 14 cwt. of coal. In large works the charging is mechanical and there are several types of charging machines available. The de Brouwer type projects the coal into the retort from a rapidly travelling belt, while the Arrol-Foulis type inserts the coal as a series of seven or eight consecutive "shots" of about 100 lb. each from each end of the retort. When the charge of coal is in, the doors are shut and fastened, and left for ten hours. During that period the coal acquires a temperature reaching  $1,000^{\circ}\text{C}$ . and is converted to coke. Gas, tar, ammonia, water vapour, and other impurities pass through the offtake pipes and are continually pulled away by the vacuum supplied to the collecting mains by the exhaustor (see later). At the expiration of the ten-hour carbonising period



(By courtesy of Messrs. Draken Ltd.)

FIG. 170. Horizontal Retorts with Congdon Scrubber Stand Pipes.



(By courtesy of Messrs. Draken Ltd.)

FIG. 169. Horizontal Retorts with Ascension Pipes.



The doors are opened and the residual coke expelled by means of a telescopic ram. The red hot coke may be quenched in one of several ways. With the cleuve system the coke falls into a rapidly flowing stream of water which both quenches it and removes it from the retort house. Separation of the coke and water is effected by means of a sloping screen, or by a rotating selector wheel (not unlike a mill-wheel) which scoops the coke out of the stream. Alternatively, the hot coke is allowed to fall on a chain conveyer where it is sprayed with water from stand-pipes, or it may be allowed to fall into a quencher-box where again a water spray is applied.

Gas is conveyed from the retorts via the offtakes at each end in two distinct manners. The more usual method is by means of ascension pipes (as illustrated in Fig. 169) which dip over at their upper ends and are sealed in liquor flowing in the hydraulic mains. A more recent development is the Congdon scrubber stand-pipe system which is illustrated in Fig. 170. In this the gas passes from the retorts offtakes through a flap valve into a square section pipe, down which is flowing a spray of liquor. The gas passes upwards against the spray, is cooled, the tar partially condensed out of it, and then pulled away through the exhausters. Condensed tar and liquor pass out of the stand-pipes through foot seals to the separator and circulating tank.

(2) **Continuous Vertical Retorts.**—These are a comparatively modern development and are economical in operation. As the name implies, the retorts are set up vertically, and the coal slowly passes through in a continuous manner, being converted to coke in the process. Fig. 171 is a diagrammatic sketch of this type of plant. Coal enters via a gas-tight coal valve from an intermediate hopper fitted to the top mouthpiece of the retort, and the residual coke is extracted by means of a mechanical extractor at the base. The speed of the coke extractor determines the rate at which coal passes through the retort, and this speed can be varied by a simple mechanism to ensure that the coal is completely carbonised by the time it reaches the bottom. The coke discharged by the extractor is received and temporarily stored in a coke receiving chamber, from which it is periodically discharged through a gas-tight door.

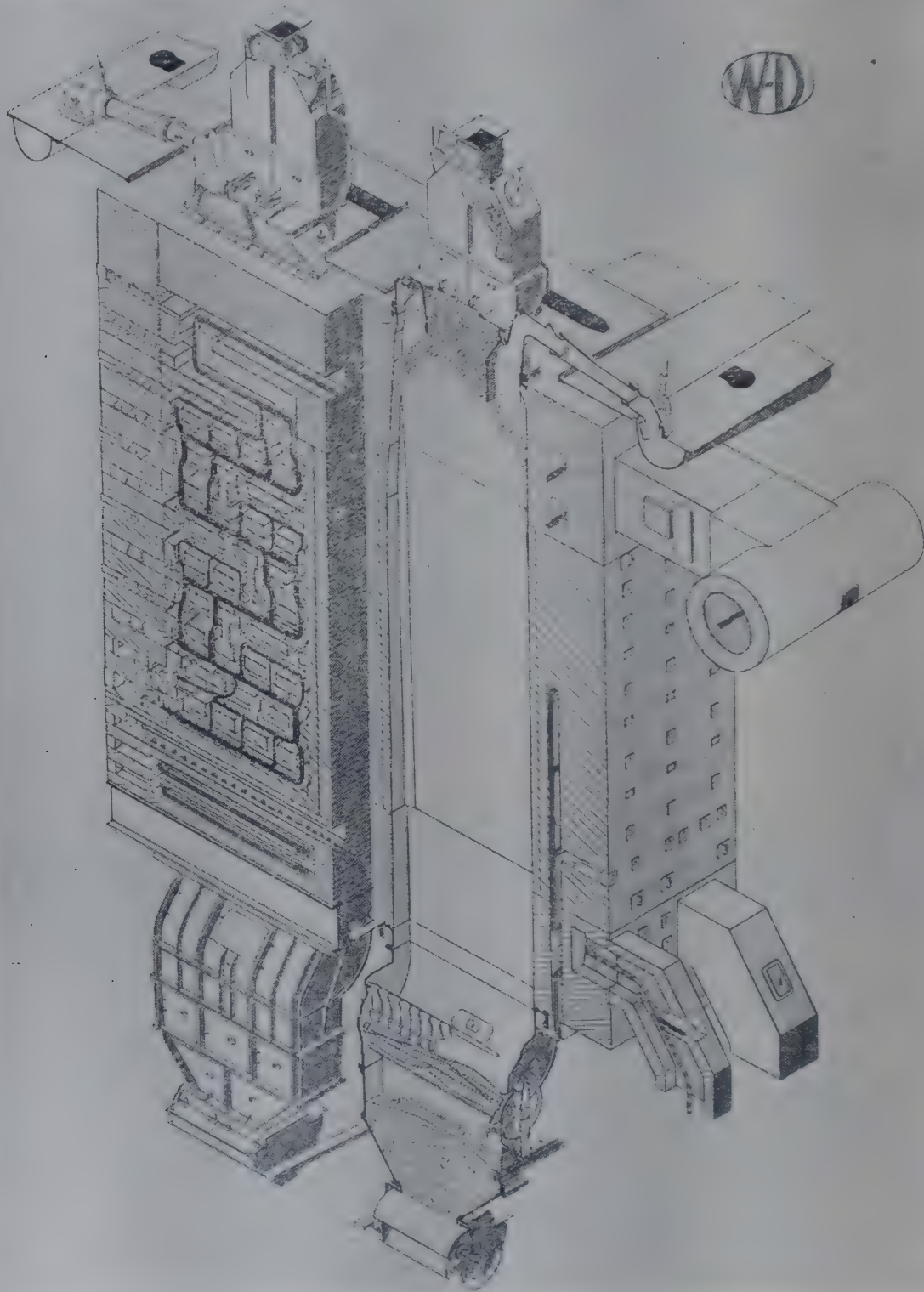
The retort is usually some 25 ft. high and is heated by producer gas flames travelling horizontally or vertically in the combustion chambers. Steam is admitted in controlled quantities at the base of the retort. This steam reacts with the hot coke to form water gas, thus increasing the gas yield. As the reaction,  $C + H_2O \rightarrow CO + H_2$ , is endothermic, the steaming process assists in the quenching of the coke. The gas obtained from vertical retorts has a lower calorific value and is generally more paraffinic than that from horizontals. This is largely because a high proportion of the gas is released from the coal in the upper part of the retort where the temperatures are not high enough to "crack" the primary products. Arrangements of offtakes and connections to the vacuum mains are seen from the diagram (Fig. 171), and are generally similar to those on horizontal settings with ascension pipes.

(3) **Intermittent Vertical Chambers.**—Intermittent verticals fall in many respects between the horizontal and the continuous vertical retort. The vertical chambers are usually rectangular and are charged from overhead coal hoppers by gravity. At the end of the carbonising period the coke is released through a bottom door. In some designs a downwards extension of the chamber below the heating zone forms a dry quenching compartment; when a quenched charge is extracted the hot coke from the heating zone descends to be quenched, and a new charge of coal is admitted. In other designs the whole coke charge is dropped into a quenching car, carried away in it, and sprayed with water under a quenching tower. The sketch (Fig. 172) shows a plant of this type. Gas offtakes are provided at the top and bottom of the retort and provision is made for steaming during the last hour or two of the carbonising period, steam generally being admitted at the bottom of the chamber and the bottom offtake closed. The



properties of the products lie in general between those of continuous verticals and horizontals.

The foregoing types of plant are those most widely used in Great Britain



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*[The Woodall-Duckham Co. Ltd.*

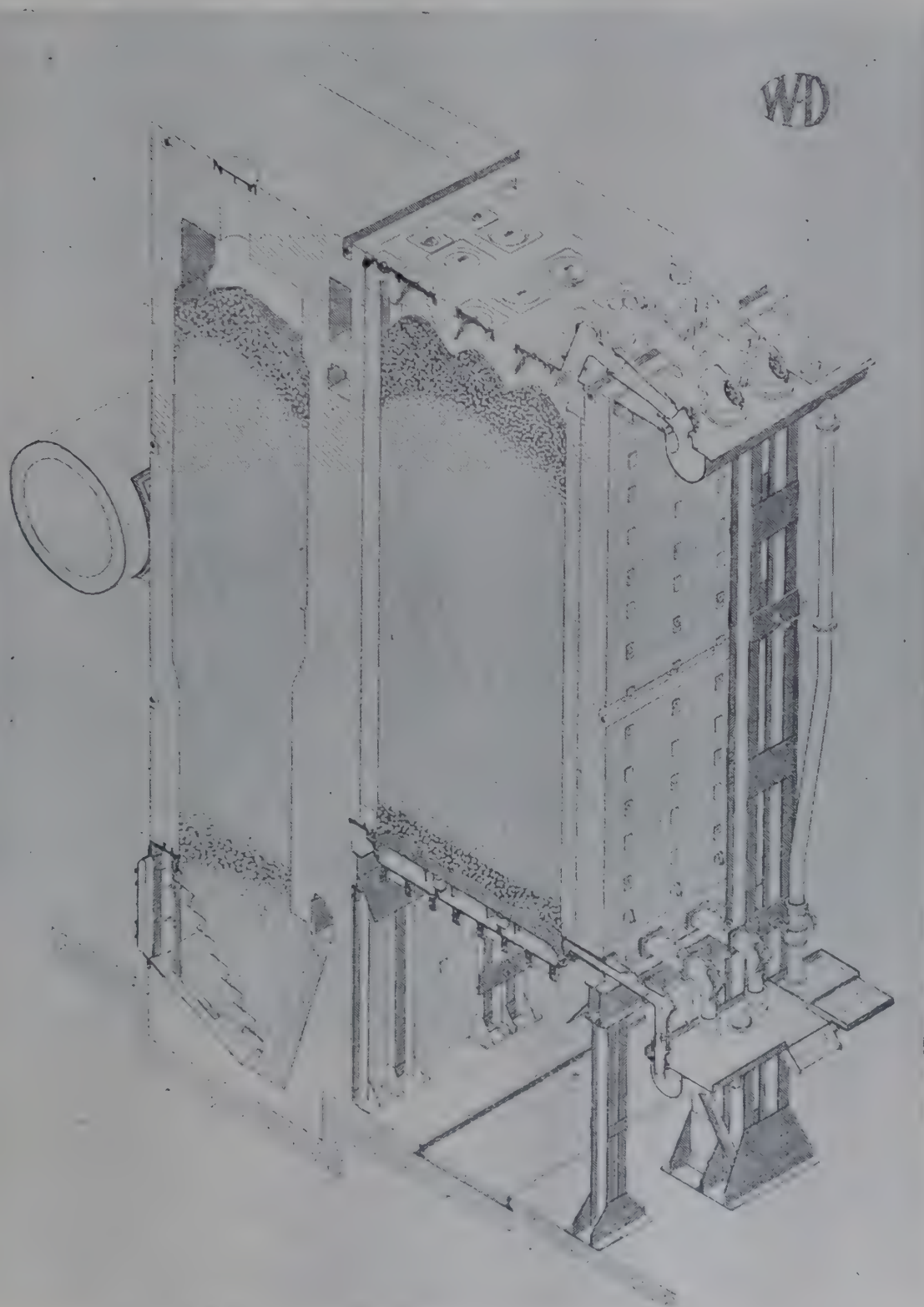
FIG. 171.—Cut-away Diagram of the W-D Lambent-Heated Continuous Vertical Retort.

for making coal gas for towns' use. There are numerous modifications to the units described, and many works combine one or more types with water gas plants or producers.

**Coke Ovens.**—In the two decades following 1930, however, another type of plant came into prominence for the production of coal gas. This was the by-product coke oven. Metallurgical coke was originally made in bee-hive ovens



in which heaps of coking coal were heated by internal combustion. Gas and other products were allowed to go to waste. In 1882 the first by-product coke



*Reproduced by courtesy]*

*[The Woodall-Duckham Co. Ltd.*

FIG. 172.—Cut-away Diagram of the W-D fully-recuperative Intermittent Vertical Chamber with built-in step-grate Producers. Section showing Chamber and Producer.

ovens were erected in this country, and great strides have been made since that date. The modern battery may contain twenty or more ovens in a group. Each oven may be 15 in. to 20 in. wide, 12 ft. or more high, and over 40 ft. in length. The ovens are arranged parallel to one another and the dividing walls form the heating flue. They are charged from a coal car on the top, and the coke discharged

by removing the end doors of the oven and pushing the coke out at one end by means of a mechanical ram. The gas, tar and benzole are similar to those obtained from horizontal retorts, and the coke is hard and dense. In the steel works the gas is a by-product, part of it being used to heat the ovens and the rest either used as a fuel on the works or sold to the local town's gas undertaking. In the past much of this gas was blown to waste, but to-day its value is undisputed. In Sheffield, for example, some 80 per cent. of the gas supplied to the public comes from by-product coke ovens. In some cases blast furnace gas or producer gas



*Photo by courtesy]*

*[Simon Carves Ltd.*

FIG. 173.—Ram side of large Coke Ovens Installation.

is used for oven heating, thus giving a higher yield of disposable coal gas. Coke ovens fired with producer gas are installed at some large gasworks (*e.g.*, Beckton and East Greenwich in London), and here coal gas is the primary product and coke the by-product. The illustration (Fig. 173) shows the ram side of a large coke oven battery in the north of England.

## WATER GAS

Water gas is widely used in Britain to supplement the supply of coal gas for towns' use. Although its production is in general more costly than that of coal gas the plant can be brought into use from cold at comparatively short notice. Hence it is invaluable for meeting sudden demands during periods of cold weather.

**Blue water gas**, resulting from the reaction between incandescent coke and steam, is a mixture of carbon monoxide and hydrogen with a small percentage of inert constituents, and has a calorific value of nearly 300 B.Th.U. per cubic



foot. Its calorific value may be increased by almost any desired extent by "cracking" oil, which is sprayed on to red hot checker brickwork over which the blue water gas is passing. The resulting mixture of gases is **Carburetted water gas**. Both blue water gas and carburetted water gas have a higher density than coal gas, and if mixed in varying proportions with coal gas the density of the mixture will vary. Variations in density may cause burners to light back or work inefficiently, and this is an objection to the indiscriminate use of water gas. During the coal shortage of 1947, however, when gas oil was readily available, many carburetted water gas plants were on base load, peaks being taken by the coal gas plants.

Water gas plants may be used to some extent to balance makes and sales of coke. When the demand for coke falls, a higher proportion of water gas is made; this has the double effect of reducing the coke made in the coal gas plant and increasing the coke used in the water gas plant.

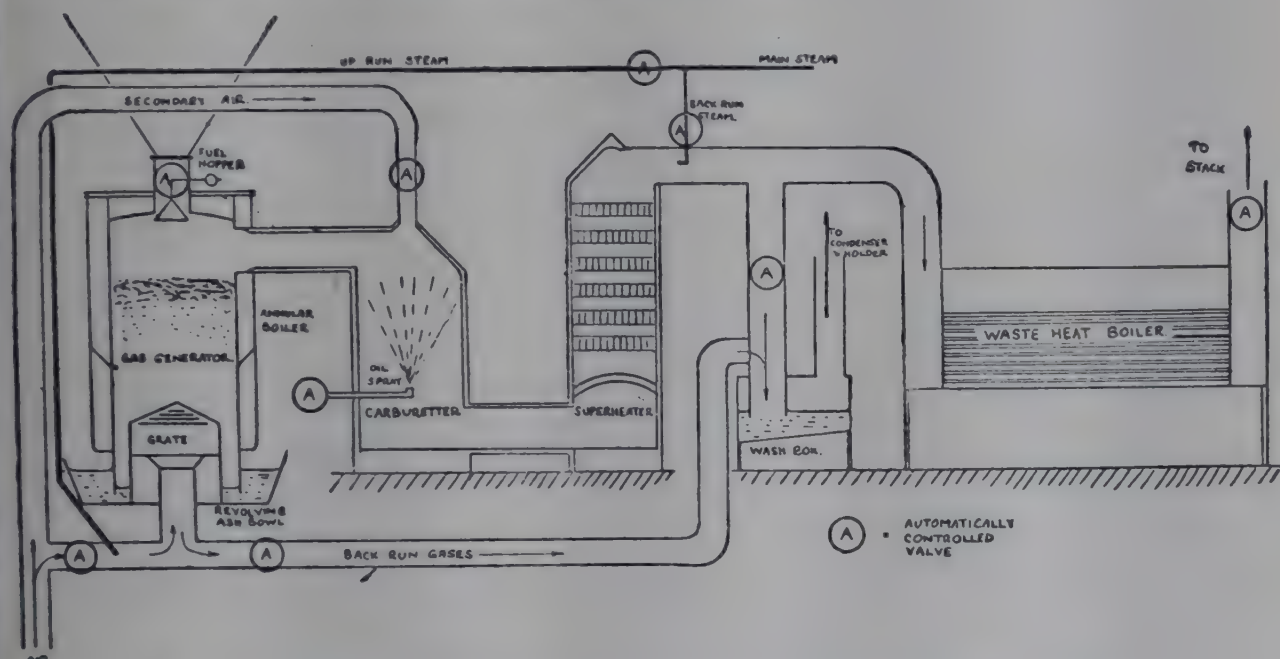


FIG. 174.—Simplified Diagram of an Automatic Carburetted Water Gas Plant.

The sketch (Fig. 174) shows a typical water gas plant. It consists of a generator (a steel vessel with a brick lining or with an annular boiler built round it), a carburetter, and a superheater, the last two vessels being always brick lined. The generator contains the fuel bed (coke) which decomposes the steam to give blue water gas (B.W.G.). The carburetter receives the spray of enriching oil and vapourises it, and the superheater decomposes the oil vapours to gaseous hydrocarbons. A water sealed wash box is provided to act as a non-return valve, preventing gas from the holder passing back into the superheater during the "blow."

The manufacture of C.W.G. involves three main stages in a cyclic process. These stages are as follows:—

(1) *The Blow*.—An air blast is supplied which passes up the generator, down the carburetter, up the superheater, through the waste-heat boiler, and out of the stack. Owing to the depth of the fuel bed in the generator the blow gases leaving it have the composition of a poor producer gas. These gases are burned by the admission of secondary air at the top of the carburetter, the zone of combustion extending through the carburetter and the superheater. At the end of the blow all air supplies are stopped.

(2) *The Up-run*.—The blow raises the temperature of the fuel bed, the carburetter, and the superheater. It is followed by the up-run steam which is admitted at the base of the generator. Blue water gas is formed. After a few



seconds purge the stack valve shuts and the oil spray is turned on. The gases are then forced down the carburetter, up the superheater, down through the wash box, and on to the holder.

(3) *The Back-run.*—In order to keep the reaction zone in the generator from rising too high in the fuel bed the final phase of the process, known as the back-run, is introduced. In this, steam passes down through the generator, the up-run steam being shut off, and the B.W.G. so generated travels along the bottom by-pass line to the wash box and so to the holder. The valve in the main connecting the top of the superheater to the wash box is closed during this stage. At the end of the back-run the fuel and the other vessels have cooled and the blow follows to restore their temperature.

In most large plants all valves work automatically from a master controller which ensures that the right sequence is observed, thus avoiding the danger of an explosion. The duration of a complete cycle is usually about three minutes, divided into: blow, 55–70 sec.; up-run, 55–90 sec.; and back-run, 35–55 sec.

**Waste-heat Boilers.**—From horizontal and vertical retorts, from vertical chambers, and from water gas plants steam is often raised by making use of the sensible heat of the flue gases. These hot flue gases are passed through the fire tubes of a boiler, and in doing so are reduced in temperature by some  $200^{\circ}$ – $600^{\circ}$  C. From a bench of 150 horizontal retorts about 10,000 lbs. of steam per hour at 160 p.s.i. may be raised in this way.

## PRODUCER GAS

**Producer gas** has a number of industrial applications. The manufacturing process is simple. A mixture of air and steam is passed through a mass of incandescent coal or coke, and at the high temperature in the producer or generator, carbon monoxide is the main product of oxidation of the solid fuel. In addition the steam undergoes the endothermic water gas reaction, and absorbs some of the heat of the oxidation. The resulting producer gas is therefore a mixture of volatile matter from the solid fuel, together with carbon monoxide, hydrogen, and unchanged nitrogen from the air. Owing to the presence of over 50 per cent. nitrogen, producer gas has a low calorific value and a high density. Thus it is unsuitable for transmission over long distances and, unless either the producer gas or the secondary air is preheated, the flame temperature is low.

There are a number of types of generator. In gasworks practice an internal producer forming an integral part of the setting provides gas for heating the retorts (see Fig. 168). These producers are fed with coke, and in the case of horizontals hot coke may be pushed straight from the retort into the producer fire, thus making for thermal economy. Internal producers may be operated by the natural draught from the chimney or by fans. Hot producer gas from the fire passes through a short flue to the combustion chamber and preheating is unnecessary, although the secondary air is sometimes heated. Steam is supplied as water which is run over the grate bars for cooling purposes; it evaporates into the primary air stream, and plays the part in the reaction described above.

Producers which are not built into the retort setting are used in some cases in the gas industry and are referred to as "external" producers. They are similar to those used in other industries. They lack the thermal advantage of a hot coke feed, but have the advantage of being more readily and easily controllable. Such producers are generally housed in a steel shell, which may be either brick-lined or form an annular boiler in which steam is raised for saturating the blast. In the Marischka producer, high pressure steam is generated for power purposes. In some types the clinker is removed by hand, but in others a revolving grate with plough attached removes the ash mechanically. Primary air is supplied under pressure from fans, and steam is added to the air to give a saturation temperature of about  $55^{\circ}$  C. The fuel, either coal or coke closely graded, is added



at intervals through a top feed hole. The gas leaving the producer is generally passed through a water scrubbing tower and sometimes other purifying plant. Even when coke is used as fuel the gas carries forward a thick tar which is often troublesome.

Besides its use for heating retorts, producer gas is often used in gasworks for dilution of coal gas to the standard calorific value. It is used in metallurgical practice and in glassworks, and small mobile producers have been fitted to motor vehicles to replace petrol and oil in times of shortage of liquid fuels.

The "slagging" producer is operated at such a high temperature that the ash from the fuel is molten and can be tapped off, the high temperature being obtained by reducing the steam added to the blast. The underground gasification of coal is virtually an example of the producer gas operation.

## SOME OTHER FUEL GASES

**Blast furnace gas**, taken from the top of the furnace used for iron production, is a low calorific value gas. It may be used for heating in an adjacent steel works or coke oven plant, but is unsuitable for transmission over a distance.

**Sludge gas** is used for power generation on sewage farms.

**Natural gas** from petroleum fields is widely used in the United States of America and elsewhere. As it possesses a high calorific value it can be piped economically over long distances.

**Uncondensable gases** from the processing of petroleum have similar applications. An example in England comes from the plant of Petrochemicals Ltd., near Manchester, where surplus gas is delivered to the local gasworks.

**Acetylene**, prepared by the action of water on calcium carbide, used to be widely used for lighting, but more is now used for oxy-acetylene welding and similar industrial purposes. It can be stored as a solution under pressure in acetone.

**Hydrogen**.—Although not used extensively as a fuel gas, hydrogen was prepared on a very large scale by the gas industry during the 1939-45 War for the balloon barrage round the larger towns and cities. It was made by the action of steam on reduced native iron ore. Reduction of the ore was effected by coal gas.

## THE PURIFICATION OF COAL GAS

Coal gas leaving the carbonising plant is normally saturated with water at a temperature of 60° C. to 80° C. It contains tar fog, ammonia, hydrogen sulphide and other sulphur compounds, hydrogen cyanide, naphthalene vapour, benzole vapour, and nitrogenous gum. All these substances should be removed from the gas before distribution. Benzole is removed because it is usually more valuable as a liquid than as a constituent of the gas. The other substances are extracted because they have corrosive or other objectionable properties. It is a statutory obligation upon public suppliers in Great Britain to remove hydrogen sulphide almost completely from the gas, but there are wide variations in the degree of removal of the other constituents mentioned.

**Exhausters**.—The gas leaves the carbonising plant by the high vacuum main. The name is misleading, for the pressure in this main is generally only a few inches of water gauge below atmospheric. The gas is drawn from the high vacuum main by exhausters, which pump it through the purification plant into the holders.

There are several types of exhausters. In the blade type the body is a horizontal cylinder with the inlet and outlet on opposite sides (see Fig. 175). A blade or blades rotating within the cylinder sweeps a volume of gas from inlet to outlet. A smaller cylinder, placed eccentrically within the body, and touching



it at the bottom, prevents the gas passing back from outlet to inlet. This is a positive type of exhauster. Another positive type is the Rootes-Connersville blower which resembles in principle the gear pump (see Fig. 186). Many modern

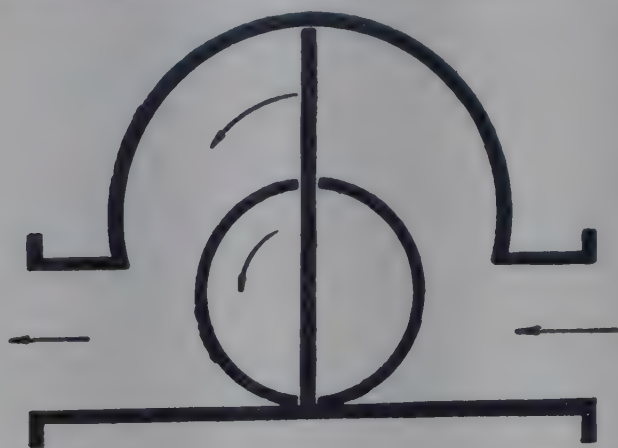


FIG. 175.—Section of Bladed Exhauster.

installations have turbo-exhausters. These high speed machines rely on centrifugal force, and occupy a much smaller ground space than the positive exhauster. The centrifugal force throws a considerable proportion of the tar fog from the gas.

Failure of the exhausters leads to a complete breakdown of the gas-making process and must be avoided at all costs. In consequence, steam power is nearly always used for driving them, and duplication of plant is usual. Exhausters are generally placed after the primary gas coolers, as they then

have a smaller volume of gas to handle.

**Condensation.**—Crude coal gas may contain from 20 to 50 per cent. of water vapour. Part of this water comes from the moisture in the coal, part results from the decomposition of the coal substance, but most of it evaporates into the gas in the hydraulic main or scrubber stand-pipes which conduct the gas from the carbonising plant.

In horizontal retorts fitted with long ascension pipes leading into the hydraulic main the gas may be cooled from  $450^{\circ}$  C. to  $150^{\circ}$  C. while passing up the ascension pipe. In this case the evaporation of a comparatively small quantity of water is all that is necessary to cool and saturate the gas. In horizontal retorts fitted with scrubber stand-pipes, and in coke ovens, gas at a temperature of  $500^{\circ}$  C. or more is brought into contact with liquor and in that case evaporates a larger quantity of water.

The cooling of the gas to atmospheric temperature and the condensation of the greater part of the water vapour is carried out in "condensers" or gas coolers. The earliest type of condenser, and which is still in use in many places, was the atmospheric one. This consisted simply of long runs of pipe, often in the form of a series of tall inverted U-bends, with the gas within the pipes and air circulating naturally outside. As in all forms of condensing plant, tar and liquor were collected in the lower part of the apparatus and run off to separating tanks.

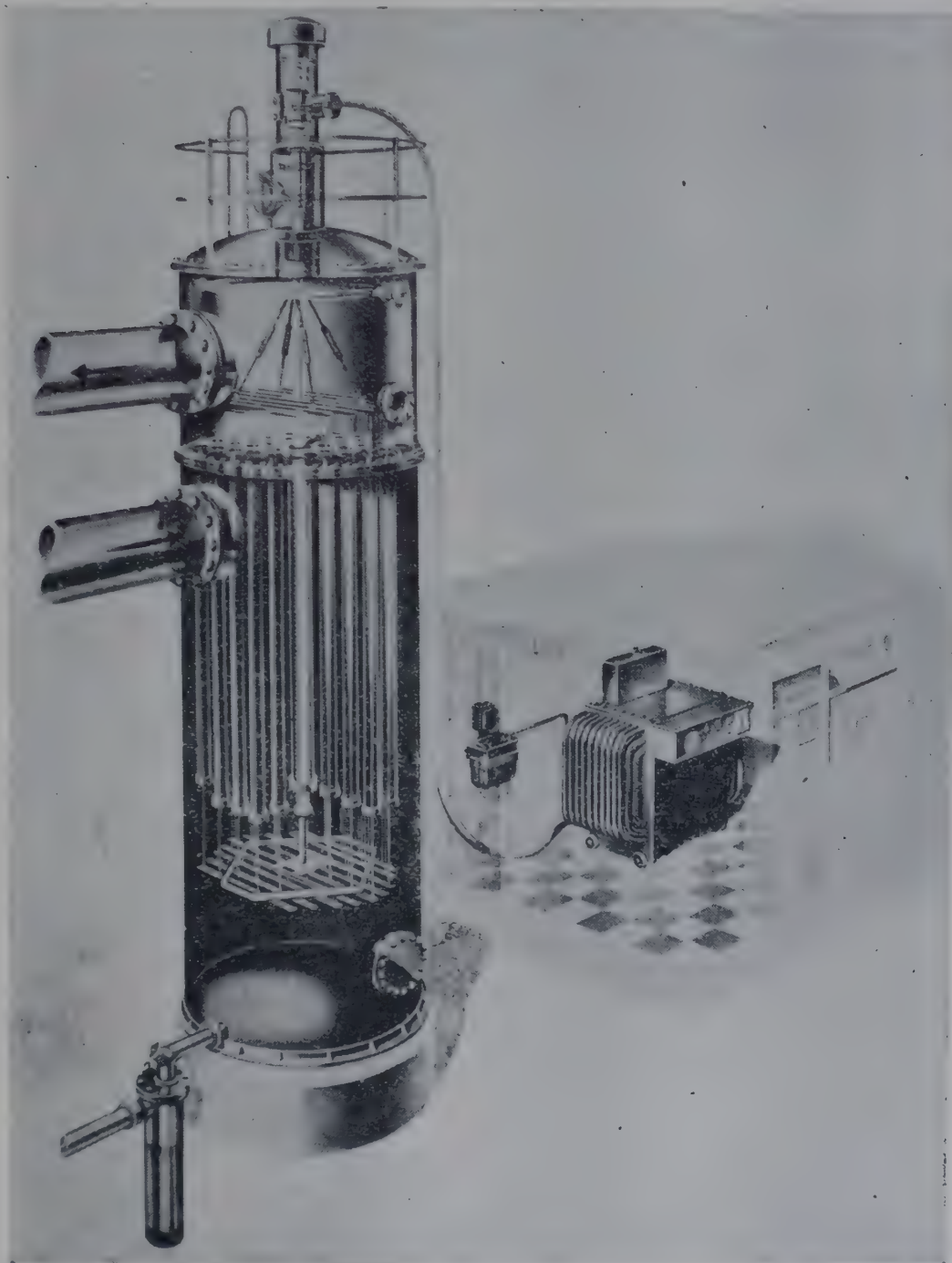
More modern condensers are water cooled. The cooling water passes through tubes around which the gas circulates in countercurrent flow. With horizontal water tubes the water is arranged to flow from bank to bank of tubes, down one side of the unit and up the other, and high water velocities are possible. The gas flows vertically across the banks of tubes, and this factor, combined with the high water velocity, leads to high heat transfer coefficients. With vertical water tubes open topped vessels are possible, and this permits cleaning of the tubes while the condenser is at work—a factor of considerable importance where muddy water is used.

When crude gas is cooled the condensate consists largely of water, although tar is deposited as well. The water dissolves a proportion of the soluble constituents of the crude gas, so that the aqueous effluent known as "virgin liquor," contains ammonia, carbon dioxide, hydrogen sulphide, hydrogen cyanide, and other substances.

Crude coal gas also contains naphthalene vapour, and this is thrown down as a solid on cooling the gas below about  $40^{\circ}$  C. Much of this naphthalene is removed with the tar, but solid deposits of crude naphthalene tend to block the gasways, particularly where the gas is further cooled in other plant following the



condensers. In some works, particularly in coke ovens practice where the semi-direct ammonia process is used (see below), the gas is cooled in two stages. The primary coolers reduce the gas temperature to about  $40^{\circ}\text{C}$ ., when the bulk of the water vapour but no naphthalene vapour is condensed. The gas then passes to the exhausters, where the compression causes a small rise in temperature. Naphthalene may then be removed by oil washing, followed by ammonia removal and final cooling in secondary coolers.



*Photo by courtesy]*

*[Whessoe Ltd.*

FIG. 176.—Diagrammatic Sketch of Electrostatic Detarrer  
(Whessoe-Woodall-Duckham Type).

**Tar and Tar Fog.**—One of the products of the carbonisation of coal is a viscous black tar. This is a complex mixture of heavy aromatic and paraffinic hydrocarbons, organic bases, and phenols, together with some free carbon. It begins to condense from the gas at a fairly high temperature, and some is deposited on retort mouthpieces, in stand-pipes, hydraulic mains, collecting



mains, and condensers. Some is carried forward in the gas in the form of a finely divided fog. In the case of positive exhausters any precipitated fog acts as a lubricant, but comparatively little is removed in this way. With turbo-exhausters the centrifugal action throws a fair proportion of the fog from the gas. Special plant is often installed for the removal of residual fog.

There are three main types of plant for the precipitation of tar fog:—

(1) Those in which the gas is subjected to sudden changes in direction, the inertia of the fog particles causing them to continue in the original direction and stick to solid surfaces. The Pelouze and Audouin extractor is an example of this type.

(2) Those in which the gas is caused to bubble in fine streams through gas liquor. The Livesey washer is of this type, which has the advantage of removing part of the ammonia from the gas as well. However, types (1) and (2) both throw a high differential pressure.

(3) Those in which the gas is subjected to a silent electric discharge. In this electrostatic precipitator (Fig. 176) one electrode is in the form of a series of vertical wires. The other electrode, which is earthed, is in the form of plates between parallel rows of wires, or in the form of tubes each coaxial with a wire—the type shown in the diagram. When the wires are subject to a negative potential of some 25,000 volts, and gas containing suspended matter is passed through the apparatus, the suspended particles receive a negative charge, and are attracted to the plates or tubes where they coalesce. Liquids such as coal tar will then run by gravity from the apparatus. The same principle may be applied to dedusting problems where the dust is dry, in which case the dust is shaken off by tapping the electrode. Electrostatic precipitation is not so successful with gummy materials, such as producer gas tar, which may be too viscous to flow (see *T. Inst. Chem. E.*, 23, 1 (1945)). With coal gas over 99 per cent. of the tar fog is removable by this means, and the plant throws a very small differential pressure. When electrostatic tar precipitators precede the condensers the virgin ammoniacal liquor is recovered from the condensers free of tar acids; it is these tar acids (phenols) that lead to some of the difficulties in the disposal of effluents when present in the liquor.

**Ammonia Extraction.**—Crude coal gas may contain over 1 per cent. by volume of ammonia, and a proportion of this ammonia is removed from the gas in hydraulic mains and stand-pipes as ammonium chloride, the chlorine being derived from chlorides in the coal. As it is comparatively insoluble in hot water the ammonia remains largely in the gaseous phase until the condensers are reached, except in the direct recovery system.

There are three main methods of ammonia extraction:—

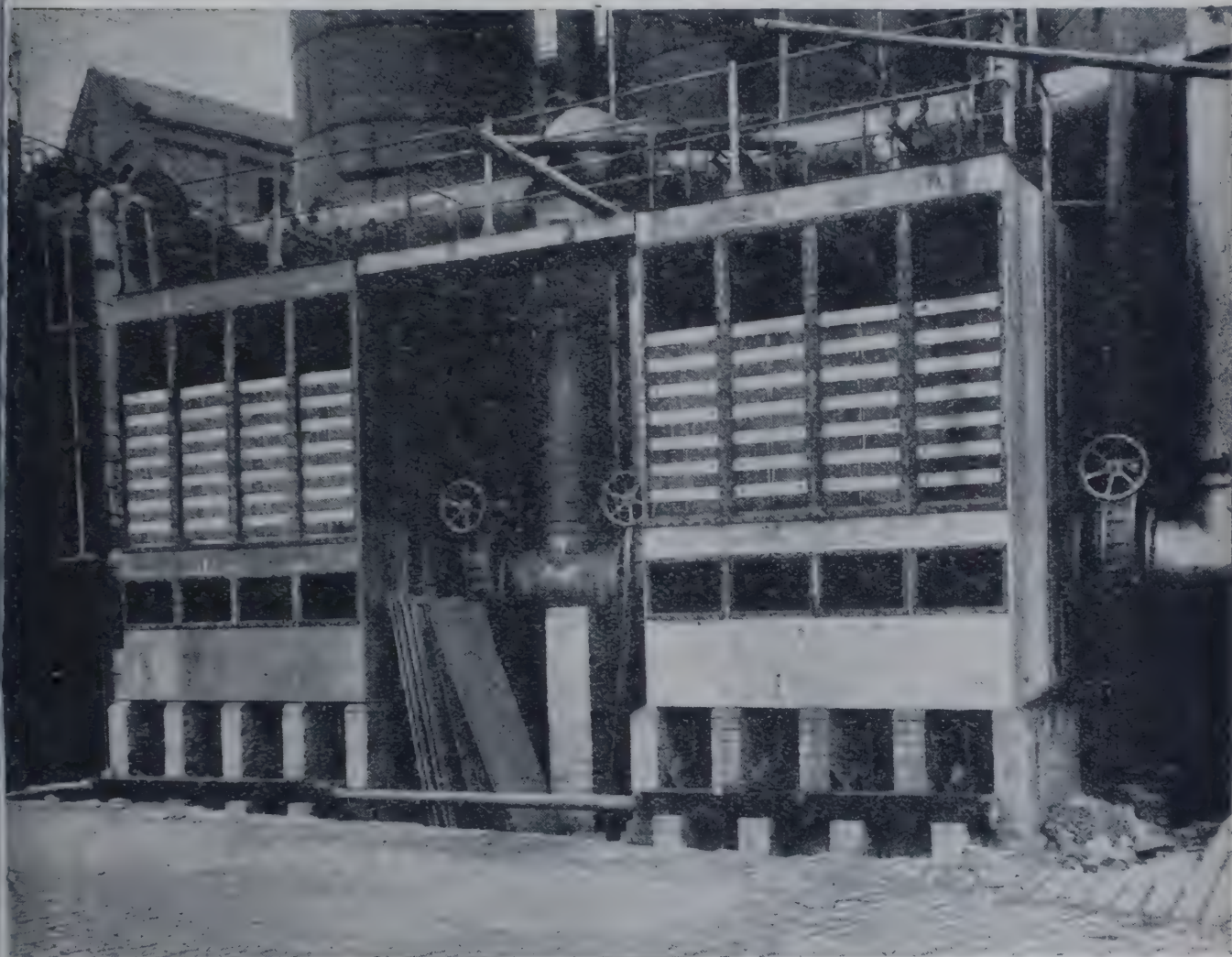
(1) *Direct recovery.*—Here the hot crude gas is passed through a sulphuric acid bath and the ammonia recovered as ammonium sulphate. The process is not widely used as tar interferes, but the electrostatic precipitation of tar from hot gas would favour the development of the scheme.

(2) *Semi-direct recovery.*—Here the gas is passed through primary condensers, where part of the ammonia is recovered in the condensate, and thence to tar precipitators. The gas then passes to a saturator containing sulphuric acid. Here it joins ammonia distilled from the virgin liquor. The acid and ammonia react to form ammonium sulphate, which crystallises out, and is separated from the acid by centrifuges. The ammonia-free gas passes through an acid trap on the outlet of the saturator. The acid seal causes a high gas pressure drop.

(3) *Indirect recovery.*—This system is adopted in most gasworks. The gas is cooled in condensers to a temperature as low as is economically possible with the cooling water available. The proportion of free ammonia recovered in the condensate depends on the outlet gas temperature. The gas then passes to the tar extractors. When these are of the Livesey washer type, they are fed with liquor from the final ammonia washers and some ammonia is removed from the gas, increasing the concentration in the liquor. From the tar extractors



the gas enters the ammonia washers. These may be in the form of two or more tower scrubbers in series, or in the form of multistage rotary or static washers. The multistage washers have between four and twelve compartments, each containing a reserve of liquor which is circulated within the compartment. The circulation is effected either by a rotating bundle for rotary washers or by an external pump for static washers. The gas passes through each compartment in turn. Water is admitted to the gas outlet compartment, overflows gradually



*Photo by courtesy]*

*[Whessoe Ltd.*

FIG. 177.—Static Ammonia Washer for treating 4,000,000 cu. ft. per day. Photograph taken during construction, showing the wooden grid packing.

from one compartment to the next, and flows from the gas inlet compartment to storage. Fig. 177 shows a multistage static washer.

Tower scrubbers may be packed with boards or coke, or stoneware shapes. Water or liquor is sprayed in at the top, and withdrawn at the bottom. Gas passes in countercurrent flow up the tower. The liquor from the final scrubber is pumped to the top of the one preceding, flowing from the first one (first with respect to gas) to storage tanks (or to Livesey washers and thence to storage).

Liquor circulation systems vary greatly, but, in general, liquor from the condensers is used for preliminary cooling of hot gas in hydraulic mains or stand-pipes. Here it is stripped of much of its free ammonia, but retains ammonia fixed as the chloride. This liquor containing fixed ammonia has a low vapour pressure with respect to ammonia, and after cooling can be used in the first stages of the final ammonia washers. In very cold weather, when the solubility of ammonia is greatest, no water is necessary on the washers as it can be replaced entirely by liquor from this source.



**Removal of Hydrogen Sulphide and Hydrogen Cyanide.**—These two substances are considered together as they are both normally removed by the same reagent.

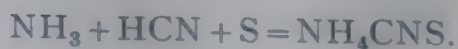
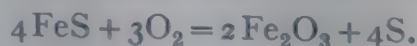
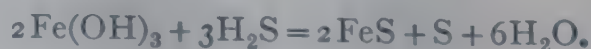
It is a legal requirement that towns' gas in the United Kingdom should be almost completely free from hydrogen sulphide. In the test laid down, a bibulous paper impregnated with lead acetate must show no darkening (due to the formation of black lead sulphide) after suspension in the gas under examination for three minutes. This corresponds to a concentration of hydrogen sulphide of less than one part per million. Although hydrogen sulphide is an undesirable constituent of a fuel gas there is no technical reason for reducing its concentration to such a low figure. Gas containing far higher concentrations of other sulphur compounds may be, and in fact are, distributed. The test is simple, and probably, when it was laid down, its sensitivity was not realised. With the traditional methods of the gas industry it was not difficult to reach the standard of purity required. Newer processes, however, are often unable to remove the last traces of hydrogen sulphide, and hence, although such methods are desirable from many points of view, development in this country has been very slow. It appears that revision of the legislation would be useful.

Some of the hydrogen sulphide and hydrogen cyanide is removed from the crude gas by the aqueous solutions in the condensers and the ammonia washers, but the gas leaving the ammonia washers may still contain about 1 per cent. of hydrogen sulphide, and perhaps one-sixth of this concentration of hydrogen cyanide. The earliest method of hydrogen sulphide removal was to pass the gas over lime contained in large purifying boxes. As carbon dioxide will displace hydrogen sulphide, it was necessary to provide sufficient lime to remove both these constituents. The calcium sulphide formed also removed carbon disulphide from the gas to form the thiocarbonate. Spent lime was objectionable to handle and not easily disposable, and during the early part of this century lime was replaced by hydrated iron oxide.

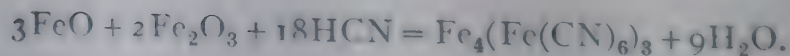
Solid ferric hydroxide reacts at ordinary temperatures with hydrogen sulphide to form a sulphide of iron, which in the presence of oxygen is revived to ferric hydroxide and free sulphur. The material can thus be used in a cyclic process until it contains over 50 per cent. sulphur, by which time its activity is so reduced that it has to be rejected. Partial revivification *in situ* is carried out whilst gas is passing through the oxide, by adding from 1 per cent. to 5 per cent. of air to the gas on the inlet of the purifying boxes, but when the material has taken up about 30 per cent. by weight of sulphur, it is removed from the box for aeration. After this aeration it is returned to the box to absorb another 20 per cent. of sulphur. On removal for the second time it is usually sold to manufacturers of sulphuric acid.

Hydrogen cyanide reacts with ferrous compounds to form complex ferrous cyanides, which are either oxidised to, or react with, ferric compounds to form ferric ferrocyanide, *i.e.*, "prussian blue." Where comparatively large quantities of ammonia pass forward to the boxes, the hydrogen cyanide may also be extracted as ammonium thiocyanate.

The reactions involved in the purification of coal gas by iron oxide are subject to some doubt, but the principal equations are:—



This reaction does not proceed directly, but represents what occurs when HCN reacts with ammon. polysulphide.



This reaction, also, probably does not proceed directly.



There are a variety of sources of iron oxide for purification. Natural bog iron ores are found in Germany and Holland, containing up to 50 per cent. ferric oxide on the dry basis. This material is imported into Great Britain in very large quantities, containing about 50 per cent. moisture as received. After partial drying it may be charged directly into the purifiers and has a good activity. Luxmasse, an artificial product, is the residue after the extraction of alumina from bauxite with soda. It contains some sodium carbonate and is highly active as a gas purifying agent. After fouling with hydrogen sulphide it is liable to fire on exposure to the air, so vigorous is the revivifying action; therefore it is often mixed with a less active material. Burnt oxide, returned from the sulphuric acid works, also forms the basis of purifying materials. This must be mixed with sawdust or something similar to increase porosity. Freshly burnt oxide has a low activity for hydrogen sulphide until it has become hydrated.

The oxide is contained in cast-iron or steel boxes, which may be 30 ft. wide by 70 ft. long on a large works, although they are generally smaller. The photographs (Figs. 178 and 179) show typical modern installations. Wooden grids are used to support the material in two or more layers up to 18 in. thick each, and the gas passes through the oxide vertically. The boxes have removable lids, fitted with rubber joints, which are taken off when the oxide has to be changed. The arrangement of the boxes is in streams of up to six boxes in series. The first four boxes in a stream are called "primary" purifiers, and the remaining boxes, if any, are referred to as "secondary" or "catch" boxes, for removing the last traces of hydrogen sulphide. The order of working the primary boxes is changed frequently, usually daily. Thus the sequence on consecutive days would be 1-2-3-4, 4-1-2-3, 3-4-1-2, 2-3-4-1, the changes in order being effected by a suitable arrangement of valves and mains. The rotation of the order of working is of benefit to revivification *in situ*, and to hydrogen cyanide removal.

In some new purification plants the oxide is contained in trays in towers. These towers take up less ground space and allow of wider application of mechanical handling, thus reducing labour costs, but the basic principle of operation is the same as for boxes. A number of processes have been devised in which liquid reagents have been used for the extraction of hydrogen sulphide, and sometimes hydrogen cyanide, from gas. Such processes have had some success in other countries, but have had little support in Great Britain because of the stringent requirements for freedom from hydrogen sulphide which obtain here. A liquid reagent must be capable of revivification, or consumption of raw materials would be prohibitively expensive, and it must be active to hydrogen sulphide but not to carbon dioxide, or the greater part of the reagent would be wasted in combining with the carbon dioxide.

Wet processes for the removal of hydrogen sulphide include:—

**The Thylox process**, in which the active material is an alkaline thioarsenate. This reacts with hydrogen sulphide to give another thioarsenate containing a higher proportion of sulphur. In the second stage of the process air is used to oxidise the reagent back to its original form, with the separation of free sulphur.

**The Ferricyanide process**, in which hydrogen sulphide reacts with an alkali ferricyanide in solution to form the ferrocyanide, which is reoxidised in the second stage of the process. Free sulphur is again the end product of the method.

**The Seaboard process**, on the other hand, uses sodium carbonate solution to remove the hydrogen sulphide from the gas, and this hydrogen sulphide is subsequently released unchanged by blowing air through the solution.

Quarendon has shown that peat, either alone or mixed with iron oxide, will react readily with hydrogen sulphide in gas, and this has been used at times when supplies of natural hydrated iron oxide have not been available, *e.g.*, in wartime.

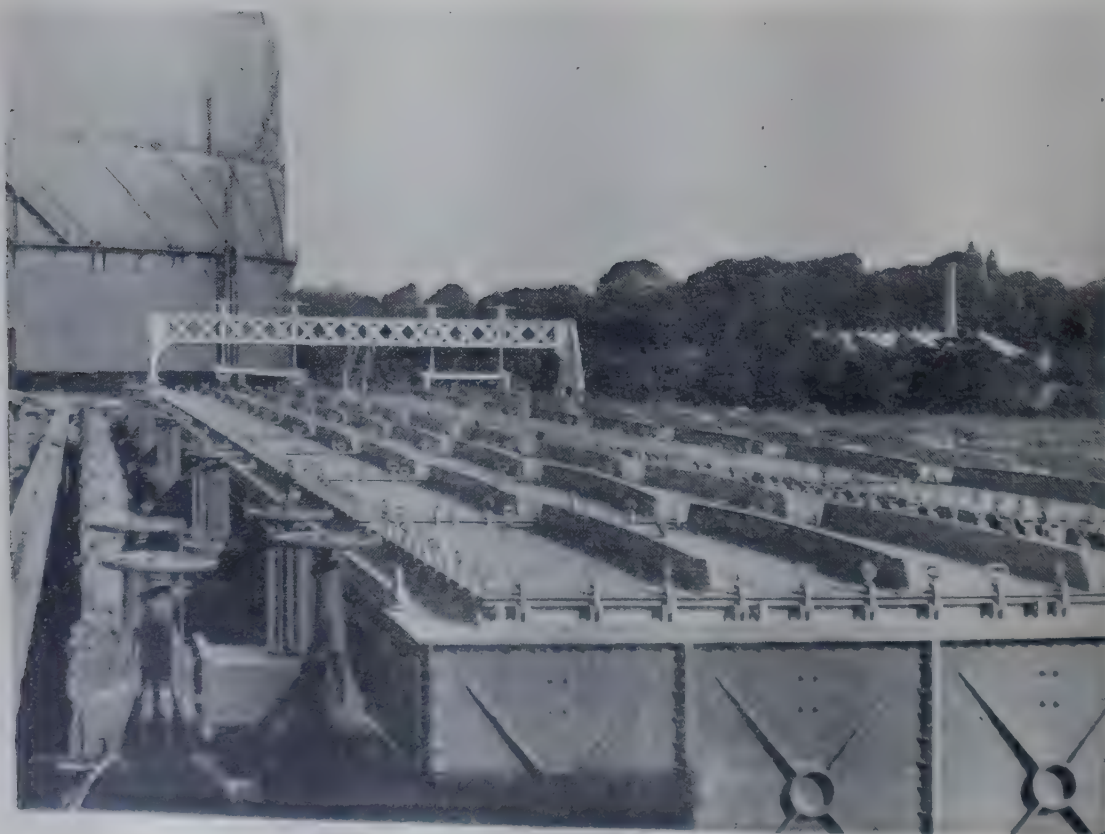




*Photo by courtesy]*

*[C. & W. Walker Ltd.*

FIG. 178.—Set of three Purifier Boxes on raised platform to facilitate discharging. Note the travelling crane for lifting the box lids and for lifting skips of ingoing oxide.



*Photo by courtesy]*

*[R. & J. Dempster Ltd.*

FIG. 179.—Ground-level Installation of Purifiers for 4,000,000 cu. ft. per day,



**The Removal of other Sulphur Compounds.**—In addition to hydrogen sulphide, coal gas may contain appreciable quantities of carbon disulphide, carbon oxysulphide, thiophen, and thiotolene, and minute quantities of other compounds such as mercaptans and thioethers, which are said to be responsible for the peculiar odour of coal gas. The objection to these sulphur compounds is that they produce sulphur dioxide on combustion, and this has undesirable physiological and corrosive properties.

The bulk of this organic sulphur is usually in the form of carbon disulphide, and an early method for the removal of this substance was the Carpenter-Evans process in which a nickel catalyst at about  $450^{\circ}$  C. caused a reduction of carbon disulphide to hydrogen sulphide, which was removable by hydrated iron oxide in the usual manner. Other oxidation and reduction catalysts have since been introduced for operation at lower temperatures, but their use has been very limited. The extraction of organic sulphur compounds with the benzole is dealt with in the next section.

**The Extraction of Benzole, Naphthalene, and Organic Sulphur Compounds.**—Benzole is recovered from coal gas for economic reasons, mainly for use as a motor fuel. About 7 per cent. of the potential heat in crude coal gas is due to its content of benzole vapour, and hence removal of the benzole leads to a substantial reduction in the therms of gas made per ton of coal carbonised. In recent years, however, the price obtained for liquid benzole has in most cases fully justified its recovery.

There are two main processes for the extraction of benzole:—

(1) **The Oil Washing process**, in which the gas is brought into contact with a light mineral oil in which the benzole dissolves. The oil is then heated and the benzole removed from it by steam distillation. After cooling, the oil is recirculated to the gas washer. This process also removes naphthalene from the gas, and if a high rate of oil circulation is maintained a substantial proportion of the sulphur compounds are taken out as well.

(2) **The Active Carbon process**, in which the gas is brought into contact with granules of porous carbon, which adsorbs condensable hydrocarbons and sulphur compounds. The adsorbed substances are removed by steaming, leaving the carbon free to adsorb a further quantity from the gas. Naphthalene is generally removed from the gas beforehand by washing with a small quantity of oil. The carbon loses its activity over a period because of the accumulation of gummy substances.

Removal of naphthalene is advisable in the case of gas from coke ovens and horizontal retorts because it condenses in solid flakes when the gas cools, and this causes blockages in pipe-lines and mains. The concentration of naphthalene in gas from continuous vertical retorts and low temperature processes is not generally high enough to cause trouble.

In the oil washing process the scrubber is similar to the types used for indirect ammonia recovery. The photograph (Fig. 180) shows a typical small distillation plant for processing about one million cu. ft. per day. The oil heaters are usually multi-tubular vessels having the oil within the tubes and steam on the shell side. In the stills oil is admitted at the top and steam at the bottom, and the mixture of benzole vapour and steam leaves at the top, passing to a condenser and separator. Stills may be ring packed, or in the larger types consist of trays with bubble caps. Debenzolised oil leaves the bottom of the still and passes through coolers before returning to the washer. These coolers are often in the form of racks with water flowing over the outside, the heat in the oil being partly dissipated in heating the water and partly in evaporating it. Considerable use is made of heat exchangers, which transfer heat from the vapours leaving the stills to the benzole-laden oil entering them. The hot oil leaving the stills is also partially cooled by exchanging heat with incoming benzolised oil.

The condensed benzole vapour is a crude product having no use as it is, but



is sold as such to the tar distillers who work it up into pure aromatic hydrocarbons or motor spirit. (See section on the Coal Tar Industry).

**Station Meters.**—The now purified gas flows through the gas-meters provided to measure the make. These meters are of two main types:—

(1) *The Wet Meter.*—This is shown diagrammatically in Fig. 185. It has the advantage that accuracy is maintained at even the smallest rates of flow. Within a cylindrical casing, partly filled with water, is a drum which is free to rotate,

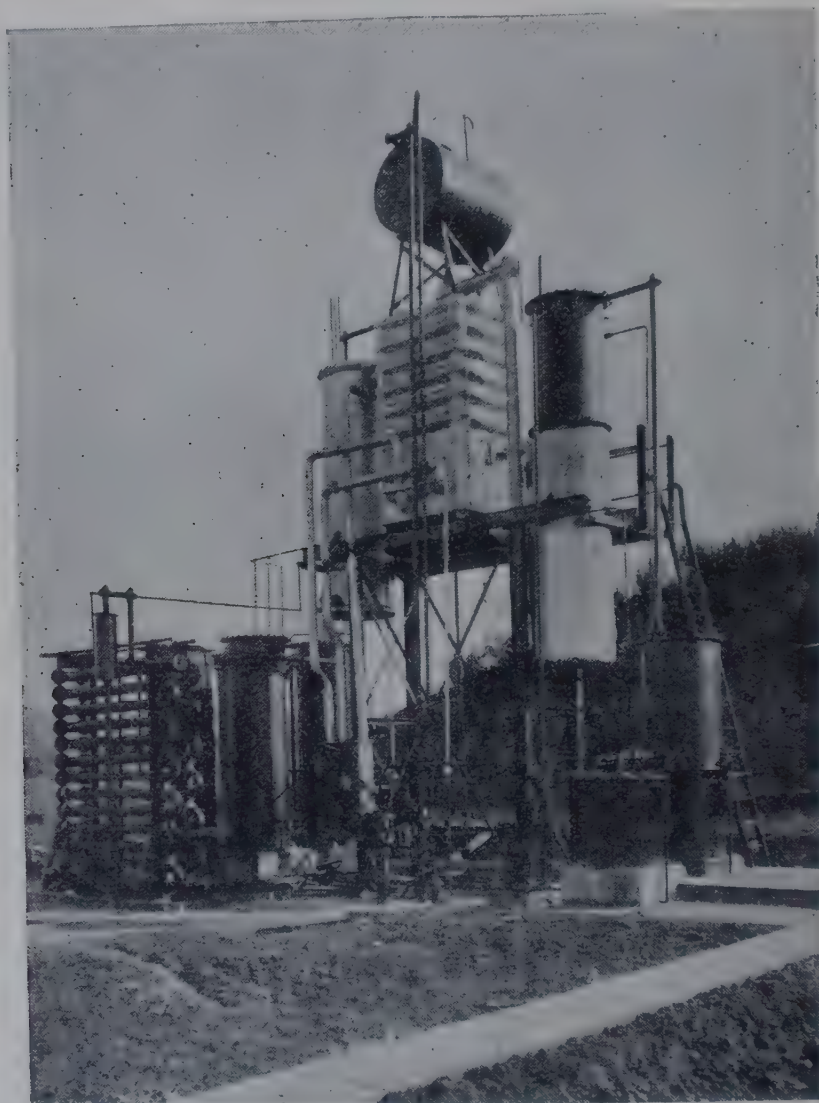


Photo by courtesy]

[R. & J. Dempster Ltd.

FIG. 180.—Crude Benzole Recovery Plant  
(Wash Oil Type).

and which has the cross section shown in the diagram. Gas enters the annular space and leaves the drum at the hub, or *vice versa*, thus causing the drum to rotate in the direction of the arrow. Accuracy of the meter depends, among other things, upon maintaining the water-level always at the same height, and this is usually achieved by means of a continuous flow of water into and out of the meter over weirs.

(2) *The Cycloidal Meter.*—This is similar to a Rootes' blower. Passage of the gas through it causes the lobes to revolve. There is a possibility of slip of gas past the rotors, but this slip is constant for a given pressure differential across the meter, and a correction may be made (see Fig. 186).

**Gas Holders.**—From the station meters the gas passes to storage vessels—gas holders. These are of two types—wet and dry. The wet holder is the older and more familiar type. It consists of an iron or steel container which



floats in a water tank. The larger holders are telescopic, each section being termed a "lift." Normally four lifts is the maximum number provided, although holders with up to six lifts have been built. Columns and framework are used in some cases to ensure that the holder floats vertically, but more recently spiral guides have been provided on the sides of each lift, so that the holders are self-aligning and the lifts rotate as they rise and fall with varying gas content (Fig. 181). Holders of the wet or water sealed type are constructed to contain up to 12,000,000 cu. ft. of gas.



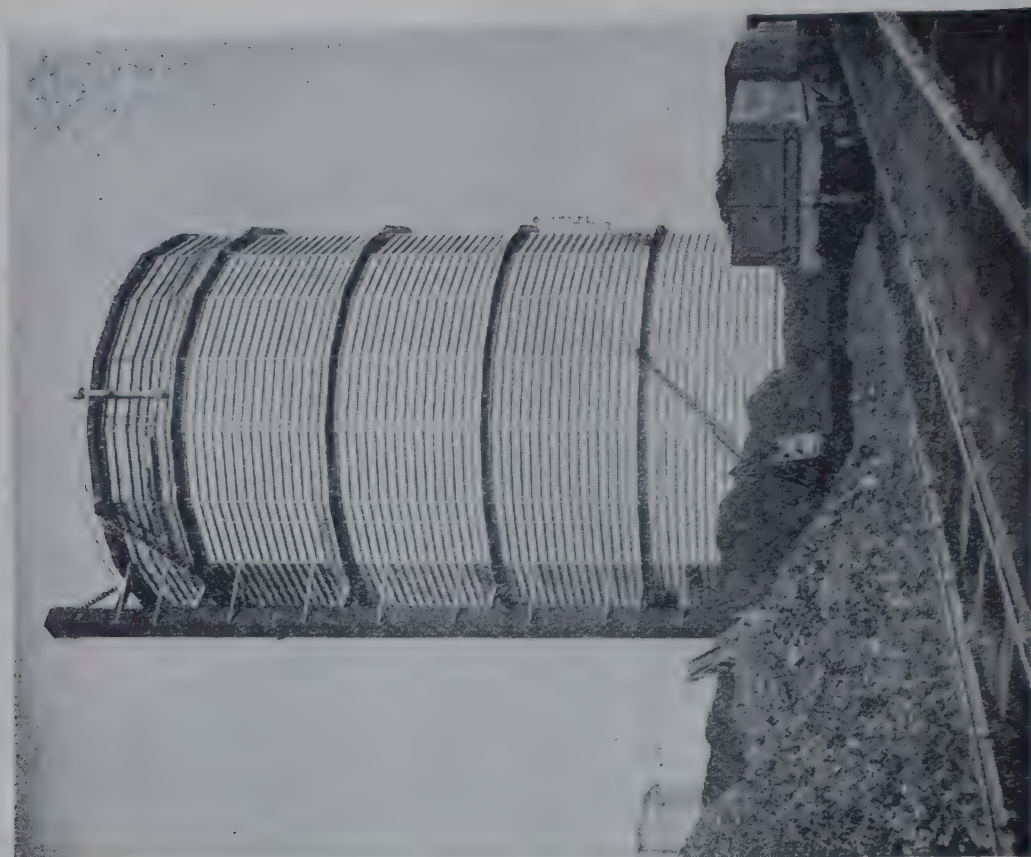
*Photo by courtesy]*

*[C. & W. Walker Ltd.*

FIG. 181.—Three-lift spirally-guided Gas Holder,  
2,000,000 cu. ft. capacity.

Dry holders are subdivided into two classes. The first consists merely of a spherical or cylindrical shell made of steel. The amount of gas it contains is regulated solely by the pressure under which it is stored (see Fig. 182). The other type is a fixed vertical cylinder with a moving piston which floats on the stored gas. The greater the amount of gas in storage the higher is the weighted piston moved. Tar is used to lubricate the piston and to keep it gas-tight. Fig. 183 shows a holder of this type.

**Dry Gas Plants.**—Some undertakings partially dry their gas, usually before storing it. This drying is effected by passing the gas through calcium chloride solution in a rotary washer similar to those used in ammonia extraction. Such dried gas has the advantage that there is no trouble in the distributing mains caused by condensed water, and that corrosion of mains and meters is reduced. Dry gas must, of course, be stored either in a dry gas holder or in a



[By courtesy of Messrs R. & J. Dempster Ltd.]

FIG. 183.—Waterless M.A.N. Gas Holder,  
2,000,000 cu. ft. capacity.

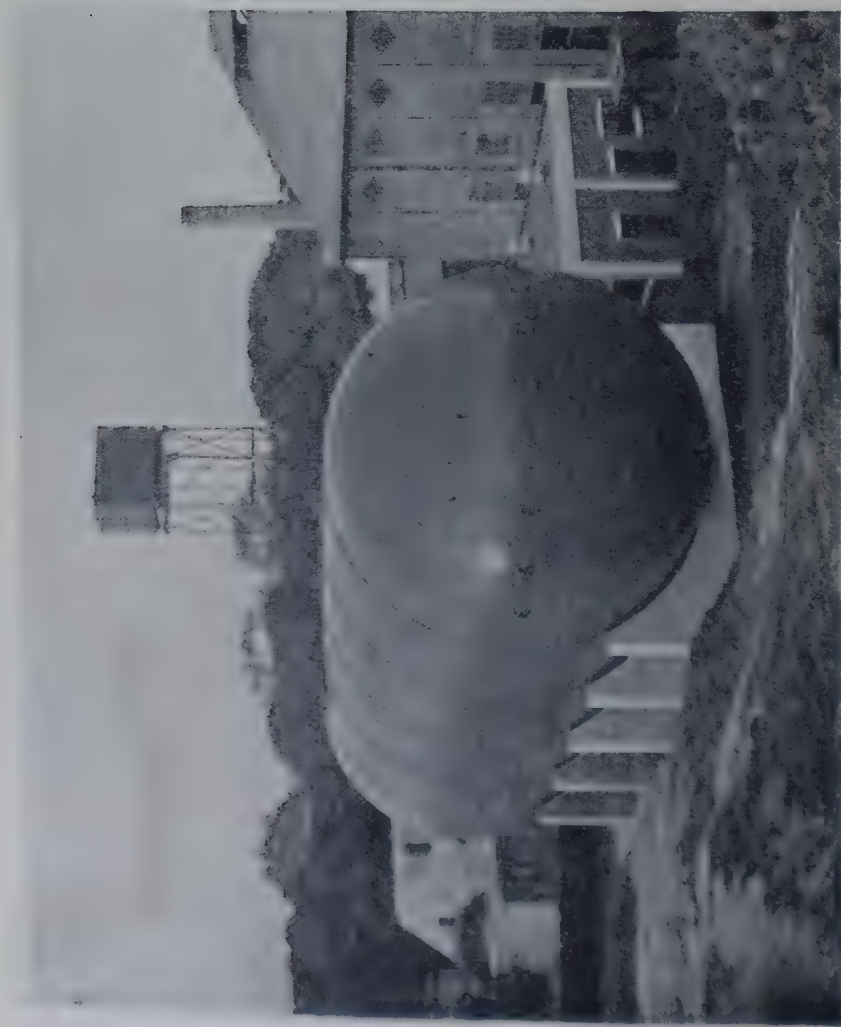


Photo by courtesy]

[Whessoe Ltd.]

FIG. 182.—Pressure Gas Holder, 187,000 cu. ft. releasable capacity.



water sealed holder in which the water surface is covered with a film of mineral oil. Occasionally dry gas plants are placed on the holder outlet, which obviates the need of oil-filming, but necessitates the installation of a gas drying plant of sufficient capacity to cope with the maximum peak load.

**Holder Water Treatment.**—The coal gas admitted to gas holders has been elaborately treated to remove hydrogen sulphide down to less than one part per million, but the purified gas in water sealed holders can be seriously contaminated with this impurity produced by bacterial reduction of sulphates in the holder water. These sulphates are reduced to sulphides which react with water and liberate hydrogen sulphide. One of the most effective ways of preventing this is to treat the water at intervals with a suspension of zinc oxide. This reagent precipitates the sulphides as insoluble zinc sulphide, which is non-reactive and falls to the bottom of the tank. Other metallic oxides or salts may be used, but they usually have the disadvantage of being electronegative to iron, and thus are not free from the suspicion that they could cause corrosion of the holder plates. Bactericides have not so far proved very successful as the concentrations required in the holder water are too great to be practicable, although if naphthalene is present in the gas bacterial production of hydrogen sulphide is rare.

**Process Control.**—There is a statutory obligation to control the calorific value of the gas supplied to the public to the declared figure. The C.V. is usually observed (on medium and large works at all events) by recording calorimeters, which trace on a tape chart the value hour by hour.

The Fairweather Calorimeter, often used for official tests, measures the C.V. by using the heat of combustion of the gas to raise the temperature of a stream of water flowing through a coil of tubing. The temperature rise is measured electrically and transmitted to a chart recording directly in B.Th.U.'s per cubic foot of gas. Corrections are automatically applied for the pressure and temperature of the gas.

Another type of recorder is the "Sigma," illustrated in Fig. 184. This instrument makes use of the heat of burning the gas to expand one steel tube relatively to another, and the movement actuates a pen tracing on a chart. Automatic devices are fitted to ensure that the flow of gas is constant, independently of pressure and temperature changes.

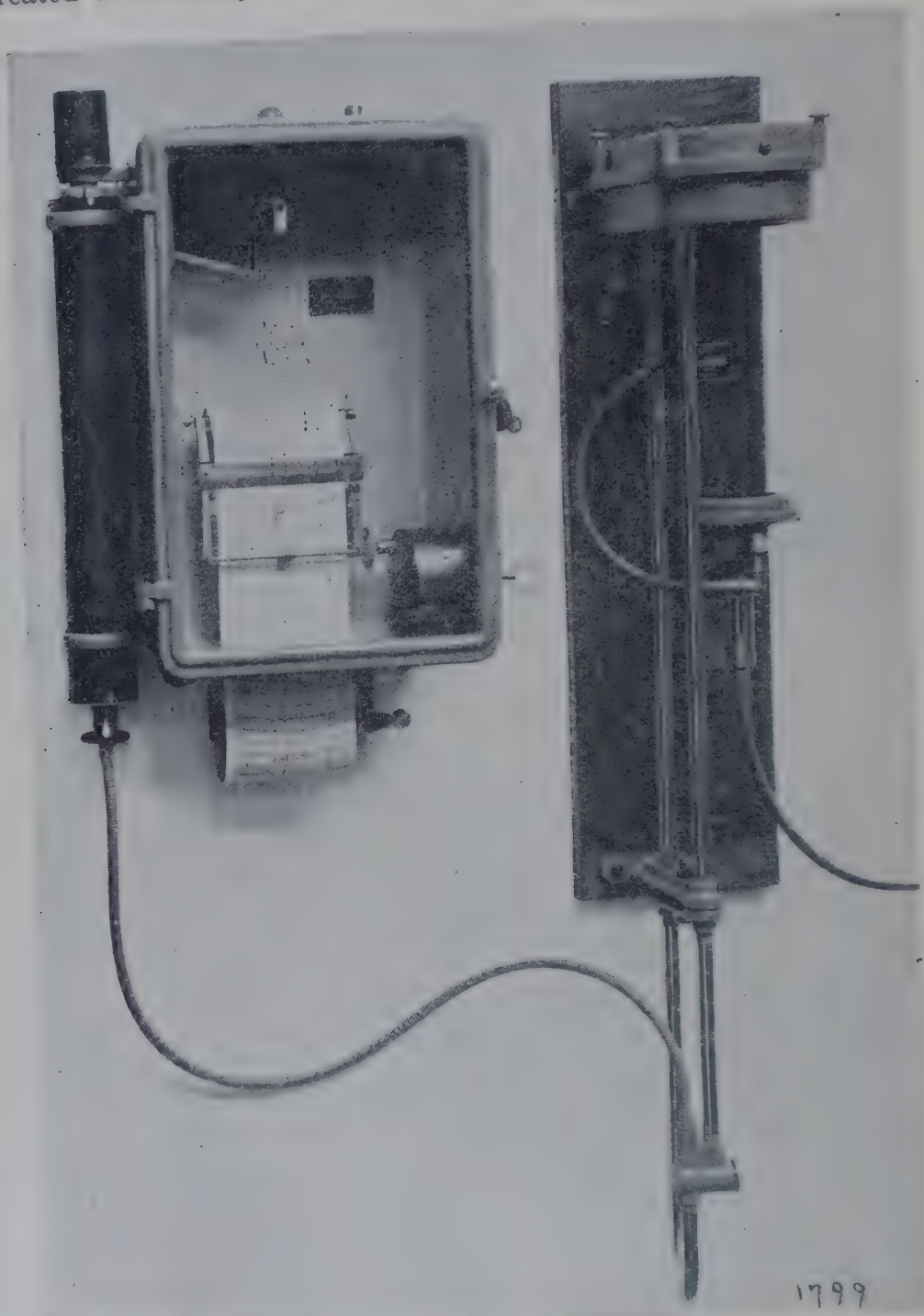
Control of the calorific value is effected in several ways. The gas may be made richer than the declared value, and diluted with waste gas, water gas, or producer gas. Alternatively, in the case of a vertical retort installation some control of C.V. may be obtained by varying the amounts of steam admitted to the retorts.

Chemical control of the process at all stages is desirable and, indeed, is essential for the efficient and economical operation of a large or medium sized works. Measurements of the combustion chamber temperatures, flue gas analyses, tests for inert constituents of the coal gas, and determinations of the efficiency of removal of ammonia, naphthalene, and hydrogen sulphide should be made as frequently as the numbers of the technical staff permit. Larger works, with more extensive staffs, also test for hydrogen cyanide removal, benzole extraction efficiency, liquor strengths, etc. Complete analysis of period samples of the finished gas is carried out as frequently as is desired.

**Gas Analysis.**—There are several types of apparatus available for the analysis of the various mixtures of gases that are encountered in the process of gas manufacture. Normally for the control of the process most needs are met by the following three types:—

1. The Orsat apparatus, which determines  $\text{CO}_2$ ,  $\text{O}_2$ , and  $\text{CO}$ .
2. The Evans apparatus, which determines nitrogen only.
3. The Constant Volume apparatus, which determines the  $\text{CO}_2$ ,  $\text{O}_2$ ,  $\text{C}_n\text{H}_m$ ,  $\text{CO}$ ,  $\text{H}_2$ ,  $\text{CH}_4$ ,  $\text{C}_2\text{H}_6$ , and  $\text{N}_2$ .

The first two are generally used in conjunction with each other. Illustrations of each type may be found in the catalogues of most scientific apparatus manufacturers. The principle of the Orsat apparatus is that a measured volume of gas is treated successively with caustic potash, chromous chloride, and cuprous



*Photo by courtesy]*

*[The Sigma Instrument Co.*

FIG. 184.—Calorific Value Recorder.

chloride solutions; the shrinkage in volume is measured after each reagent. Thus the reduction of volume after treatment with the caustic potash is due to the carbon dioxide, that after the chromous chloride due to the oxygen, and that after the cuprous chloride due to the carbon monoxide.

The Evans apparatus depends on burning a measured volume of the gas sample over red hot cupric oxide, and treating the products of combustion with caustic potash. Only nitrogen remains unchanged after this, all other constituents producing water or carbon dioxide, or both. The water condenses and the



carbon dioxide is absorbed by the potash, so that the residual nitrogen can be measured directly. The use of the Orsat and Evans apparatus is very rapid, and suitable for the routine control of the process.

The Constant Volume apparatus is more elaborate, and requires more time in its operation, but it is a very accurate instrument in the hands of an experienced operator. One form of this apparatus was described at length in the *J.S.C.I.* 57 (1938), pp. 388 *et seq.* The principle involved is the change of pressure produced when a constituent of the gas sample is either absorbed by a liquid reagent or burnt over cupric oxide under controlled conditions. The sample is brought to an arbitrary fixed volume for each pressure measurement, and corrections are

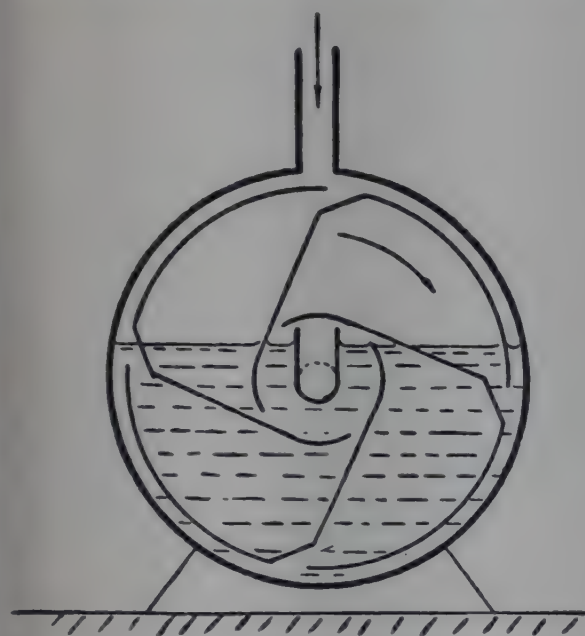


FIG. 185.—Cross Section of Wet Gas Meter.

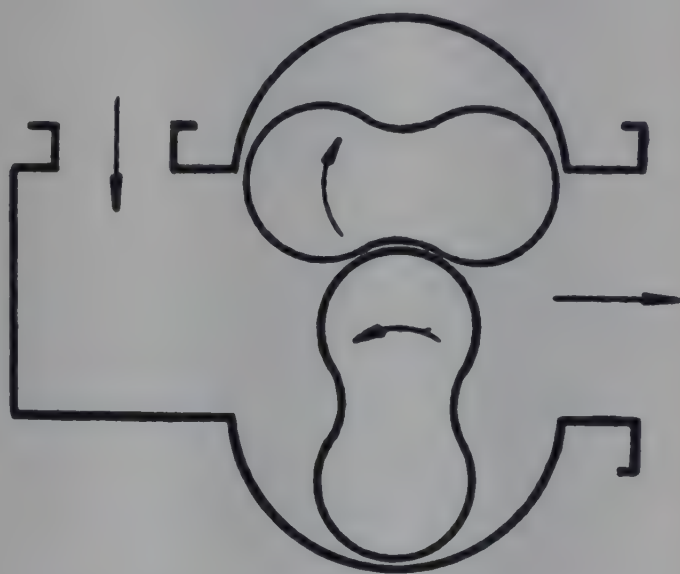


FIG. 186.—Section of Cycloidal Meter and of Roots Blower.

applied for changes in temperature and humidity. The advantage of using a fixed volume and noting changes of pressure lies in the fact that gases obey Boyle's Law much more closely at lower pressures. In this apparatus the pressure of the gas sample is initially below atmospheric, and falls still more as each constituent is removed during the course of the analysis.

### Reagents Used

**Carbon Dioxide.**—Absorb in a 30 per cent. solution of potassium hydroxide in water.

**Oxygen.**—Absorb in chromous chloride solution. Prepare by dissolving 20 g. of chromic chloride decahydrate in 52 ml. water, adding 8 ml. concentrated hydrochloric acid, and shaking the solution with an amalgam of zinc in mercury until it turns bright blue. The solution must not be exposed to the air.

**Unsaturated Hydrocarbons.**—Absorb in silver sulphate solution, prepared by dissolving 0.6 g. silver sulphate in 54 ml. of 100 per cent. sulphuric acid.

**Carbon Monoxide.**—Absorb in cuprous chloride solution, prepared by dissolving 27 g. cuprous chloride in 100 ml. concentrated hydrochloric acid, and decolorising the resulting solution by the addition of small quantities of stannous chloride.

**Hydrogen.**—Burn over cupric oxide at 270°–290° C. At this low temperature the paraffinic hydrocarbons will not be oxidised.

**Ethane and Methane.**—Burn over cupric oxide at 900° C. Methane, on combustion, produces its own volume of carbon dioxide, but ethane produces

twice its own volume. Therefore, any increase in pressure after this combustion is due to ethane. The combined methane plus ethane is determined by absorption of the products of combustion in caustic potash solution.

**Nitrogen.**—This is the residual gas after all the above steps have been carried out. Its partial pressure is read off in a manner analogous to reading the remaining volume in the Evans apparatus.

The following is a typical analysis of a straight horizontal retort coal gas after the benzole has been extracted, *i.e.*, as distributed to the public:—

Carbon dioxide	·	·	·	2.1	per cent.
Oxygen	·	·	·	0.3	„
Unsaturated hydrocarbons	·	·	·	3.2	„
Carbon monoxide	·	·	·	6.8	„
Hydrogen	·	·	·	53.6	„
Methane	·	·	·	25.6	„
Ethane	·	·	·	1.1	„
Nitrogen	·	·	·	7.3	„
				<hr/>	
				100.0	„

**Conclusion.**—The foregoing account of the Gas Industry is written in very general terms because there are very great differences in technique between one works and another. These differences arise from factors varying from matters of geographical situation down to managerial whims. Finally, the authors wish to thank the following firms for help given in the compilation of this section and for the use of photographs and diagrams used in the illustrations:—

R. & J. Dempster Ltd., Manchester.

Drakes Ltd., Halifax.

Sigma Instrument Co. Ltd., Letchworth.

Simon-Carves Ltd., Stockport.

C. & W. Walker Ltd., Donnington.

West's Gas Improvement Co. Ltd., Manchester.

Whessoe Ltd., Darlington.

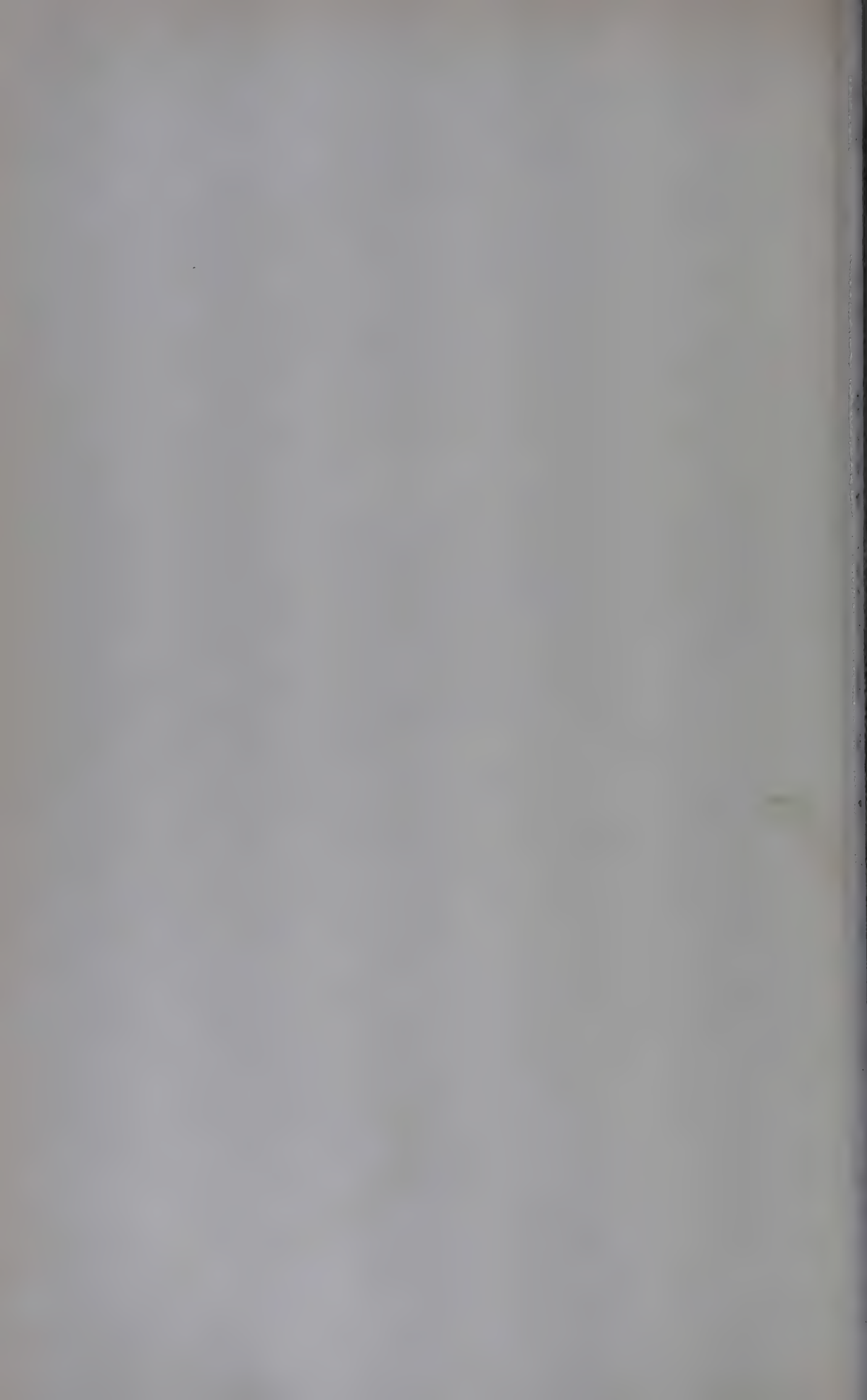
Woodall-Duckham Vertical Retort and Oven Construction Co. Ltd., London.



## SECTION XII

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### The Coal-tar Industry





# THE COAL-TAR INDUSTRY

BY ROBERT A. JONES, B.Sc., A.R.I.C.

## INTRODUCTION

THE first commercial firm established for the purpose of manufacturing coal-tar and coal-tar products was the British Tar Company, founded by Archibald Cochrane (later the 9th Earl of Dundonald), at Culross Abbey, near Edinburgh, in 1782. The main products at that date were coke, pitch and tar. The coke had a local sale to nearby iron foundries, and the pitch and tar were used by the shipbuilders as a substitute for wood-tar. The real expansion of the tar trade followed the introduction of gas lighting on a large scale in the early part of the nineteenth century, as this provided the industry with an abundance of raw material. At the same time the rapid growth of the railways produced a demand for creosote to preserve the wooden sleepers and the posts of the telegraph system. Pitch was required for briquetting coal, especially on the continent, and the invention of waterproof textiles by Charles Mackintosh created a demand for suitable rubber solvents, which was met by coal-tar naphthas. More detailed investigation and separation of coal-tar products followed Perkin's synthesis of mauve from aniline, and the subsequent rise of the dyestuffs industry in the latter half of the nineteenth century.

The total annual production of crude coal-tar in Great Britain at present is approximately two million tons, of which roughly 60 per cent. comes from gasworks and 40 per cent. from the coke ovens. The yield of tar is about 5 per cent. by weight of the coal carbonised. Practically all this two million tons is distilled for the production of coal-tar products.

In addition to crude tar, the tar distiller usually purchases crude benzole from the gasworks and coke oven undertakings, and this crude benzole, amounting to some 90,000,000 gallons a year, is also worked up into pure products.

The technique of tar and benzole distillation varies in detail with each distiller, but the outline given in the succeeding pages can be considered generally typical of British practice, without attempting to give a detailed description of the methods of any one company.

**Storage of Crude Tar.**—Most tar distillers draw their supplies of crude tar from a number of surrounding gasworks and coke oven undertakings. These crude tars vary slightly in composition, but all of them contain appreciable amounts of water in suspension, sometimes amounting to 50 per cent. or even more. To allow this water to separate, and to provide a buffer against seasonal variations in supply, large storage tanks are installed. These tanks are either of steel erected on the surface or may be in the form of brick or concrete lined wells in the ground, and contain one million gallons or more each. After the crude has settled in the storage tanks for a period, which may amount to several days or even weeks, the aqueous layer floats to the surface, and the solid particles, such as coal dust, sink to the bottom. Tar is drawn off at a point some two or three feet from the bottom of the tank, and is then fed to the stills. In this way a material is available which contains only about 4 per cent. of water, and this reduced water content greatly facilitates distillation, especially if pot-stills are used.

**Primary Distillation.**—The primary distillation splits the crude tar into a number of broad cuts which usually require further refining before being sold. The flow diagram in Fig. 187 indicates that the crude is first separated into pitch or base tar, anthracene oil, creosote oil, naphthalene oil, carbolic oil, and light oil.

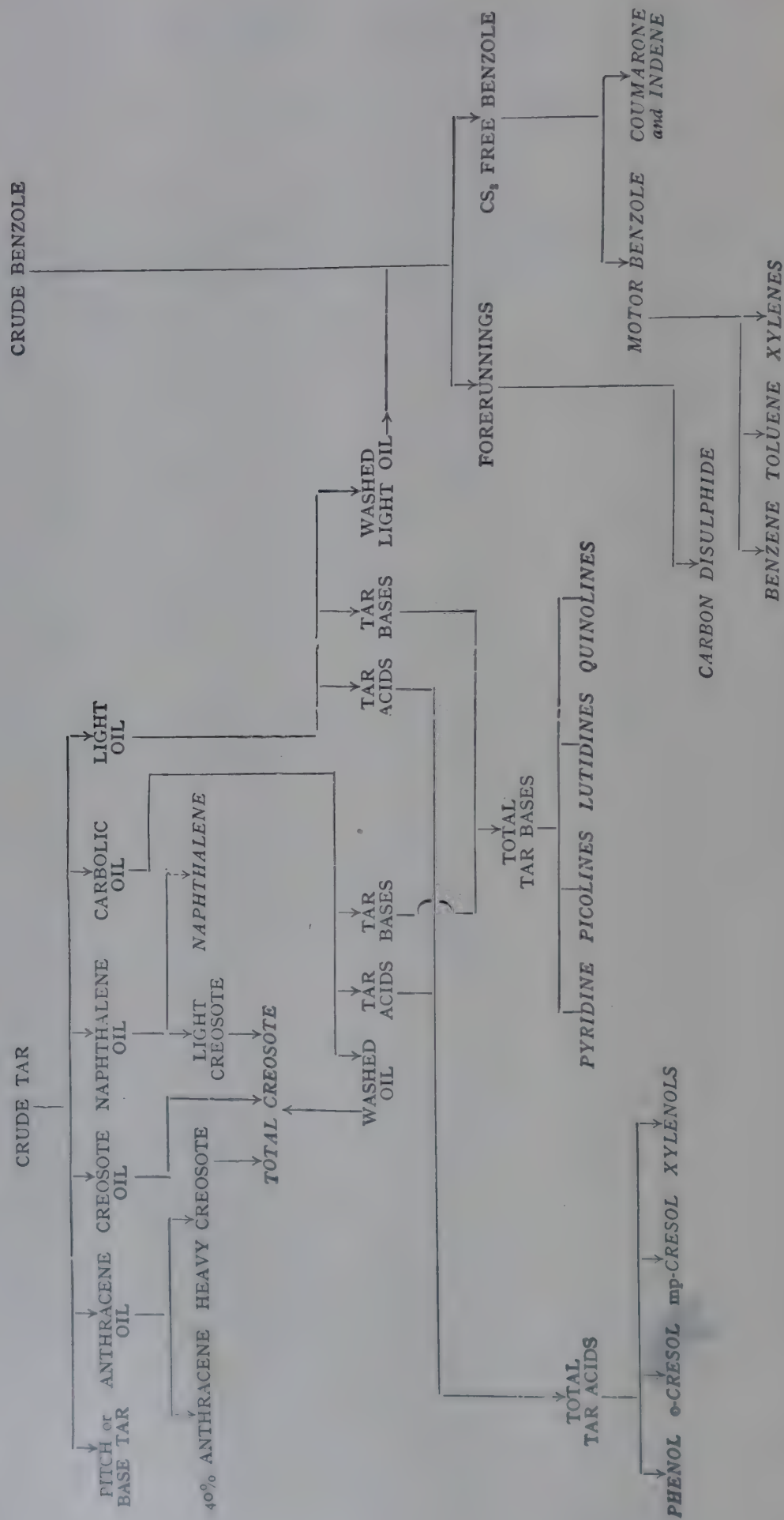


FIG. 187.—Diagram showing the Preparation of Coal-tar Products.



**Distillation in Pot-stills.**—Although continuous distillation plants have been in use for many years much of the tar distillation in this country is still carried out in pot-stills, especially by the smaller distiller. A pot-still is illustrated in Fig. 188. It is made of mild steel plate,  $\frac{1}{2}$  in. to  $\frac{7}{8}$  in. thick, and is cylindrical with a domed top and a concave bottom. The domed top is fitted with a vapour arm, safety valve, and a steam inlet. Capacities of 10 to 15 tons are commonly used. Heating is by direct firing, usually coke, and this requires very careful operation as the presence of water in the crude tar can cause serious frothing and "bumping" if heating in the early stages of distillation is too rapid. This difficulty is often overcome by installing a dehydrating unit to supply several

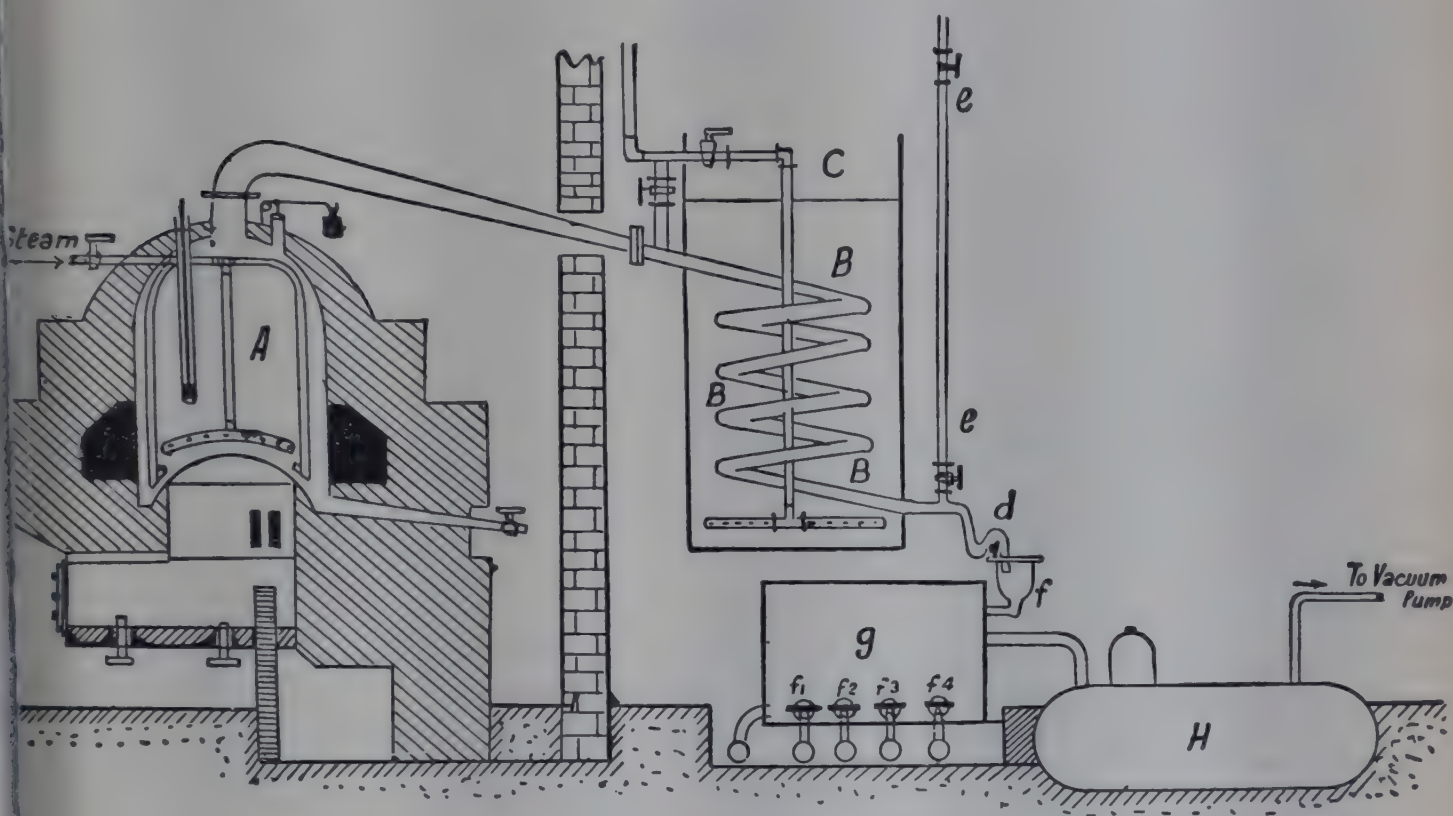


FIG. 188.—Plant for Distilling Coal-tar.

pot-stills with dry tar. An effective form of dehydrater consists of a coil of iron pipe heated in a furnace to about  $150^{\circ}\text{C}$ . Tar is passed through this coil at 40 p.s.i. and then allowed to enter an expansion box at atmospheric pressure. The water and light oils flash off into vapour. These are condensed and separated while the dehydrated tar passes on to the pot-stills.

When the still has been charged with tar the condenser tank is filled with cold water and the fire lit. The products of distillation pass through the condensing coil and into one of two receivers. The receivers are filled in turn and the contents run to the appropriate product storage tank. Steam is admitted to the still during the final stages to avoid overheating and coking the residue. The water in the condenser tank is not changed during the distillation, so that the later fractions are condensed but not cooled. This is necessary because the naphthalene and anthracene oil fractions are solids at ordinary temperatures. When distillation is complete the fire is drawn, the steam shut off, and the still allowed to cool somewhat. The residue of pitch remaining in the still is run out, while molten, into concrete bays, where it sets and is subsequently broken up for sale.

**Distillation in Pipe-stills.**—These were originally developed by the tar industry at the end of the nineteenth century, and have the following advantages over pot-stills:—



- (1) They occupy a smaller space for a given throughput.
- (2) Labour costs are lower.
- (3) There is less coking of the tar and thus they give a higher oil yield.
- (4) Wet tar is handled more easily.
- (5) There is better fractionation of the oils.

In essentials the still consists of a long length of pipe of from 1 to 5 in. in diameter, and up to several hundred feet long, arranged in the form of a series of straight sections joined by return bends. This pipe system is built into a furnace and heated by any suitable means—coal, coke, gas, or oil. Crude tar is pumped through the pipe and then to a flash chamber where it separates into oil vapours and pitch. The latter runs continuously to a cooler and thence intermittently to the setting bays, while the vapours pass to a fractioning column or to a series of fractional condensers.

Fig. 189 shows a 150 tons a day Wilton Still, and Fig. 190 shows diagrammatically the flow of materials through this plant.

Crude tar is continually pumped at the required rate from the feed tank through three heaters in series. In the first it is heated by exhaust steam from the pumps, in the second use is made of the heat of the flue gases from the furnace, and in the last one heat is exchanged with the pitch leaving the plant. The preheated tar then enters the upper section of the distillation column. Water and the light oils are vaporised, and the now dehydrated tar flows by gravity into the lower section of the distillation column. Here it mixes with hot pitch which is continuously circulated between the pipe-still and the column. The rate of recirculation of the pitch is about seven times that of the rate of feed of crude tar, so that sufficient heat is picked up by the pitch on each passage through the pipe-still to vaporise most of the remaining oils in the dehydrated tar.

When the pitch reaches the bottom of the distillation column it is picked up by the circulating pump, sent through the pipe-still to restore its temperature, and then into the central section of the distillation column. Here it meets a controlled quantity of superheated steam which removes the remaining oils and adjusts the melting-point of the pitch. At the bottom of the middle section of the distillation column is a "run-off" valve which automatically allows pitch to flow to the cooling bays in an amount proportional to the rate of feed of crude tar. The excess of pitch overflows into the bottom section where it meets the incoming crude tar and is recirculated.

The vapours are mixed and enter the fractioning column near its base. This column has some 30-40 plates of the bubble cap type. The temperature of the vapour on the top plate is automatically kept constant by a temperature controller which regulates the amount of reflux returned to the top of the column. The heaviest oil fraction leaves the column through a seal pot on the bottom plate, the intermediate products are taken off the column as side-streams, and the most volatile product (the light oil) is the excess which overflows the reflux reserve tank.

There are other types of continuous tar stills in use in this country, but, in general, the principle of operation is similar. One of the difficulties of design is to avoid coking the tar on its passage through the heating coils. In the earliest type of pipe-still—the Lennard—this is overcome by heating the coil entirely with convected heat from the furnace, and by not exposing it to radiant heat at all. Wilton's employ the recirculation principle as detailed above, and so maintain a rate of flow through the coil fast enough to avoid carbonising the tar and pitch. The Foster-Wheeler still uses a radiant furnace to heat the coil, but relies on the design of the plant to ensure that no overheating can take place.

The separation of the mixed vapours is effected either by a fractioning column as in the Wilton and the Foster-Wheeler units, or by fractional condensation with or without reflux as in the Kopper's and the Lennard stills.





*Block by courtesy]*

*[The Chemical Engineering and Wilton's Patent Furnace Co. Ltd., Horsham.*

FIG. 189.—150 Tons a Day Wilton Still.





The diagram shown in Fig. 191 indicates the boiling ranges of the products obtained from the primary distillation in the Wilton unit illustrated in Fig. 189, and is a good example of the excellent separation given by a modern continuous tar still.

### Working up the Products of the Primary Distillation

**1. Pitch.**—The tar distiller divides pitches into three main grades according to their viscosity. Soft, medium-soft, and hard are the commercial names given to these three grades, and they correspond to softening-points of  $40^{\circ}$ – $65^{\circ}$  C.,  $65^{\circ}$ – $85^{\circ}$  C., and  $85^{\circ}$ – $105^{\circ}$  C. on the ring-and-ball test. The softening-point of a pitch is altered by adjusting the amount of steam admitted to the distillation column of a continuous still, or by varying the amount of oil distilled off when pot-stills are used. Alternatively a pitch can be fluxed with a calculated quantity of heavy creosote oil to reduce its softening-point to any desired figure.

**Soft Pitch** is largely used in the manufacture of roofing felts and as a binder in the waterproofing of flat roofs. Recently soft pitch has also been used in conjunction with suitable fillers as a flooring material.

**Medium-soft Pitch** is produced in very large quantities, and the main outlet for it is in the briquetting of fine coal. About 5–10 per cent. by weight of pitch is used, and the plastic material so formed is compressed into regular shapes while warm.

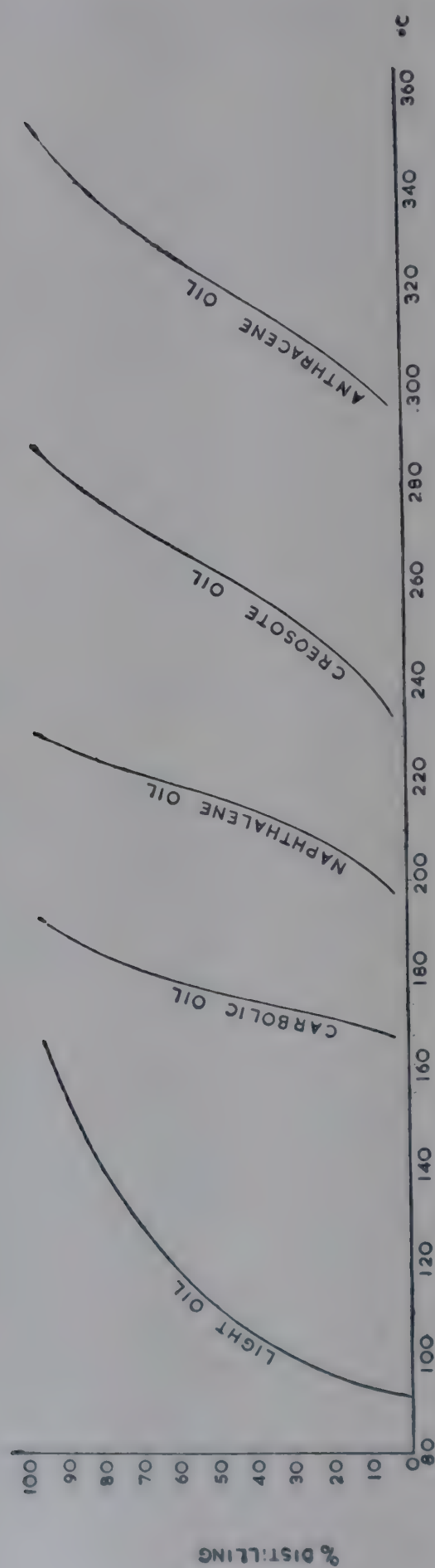
**Hard Pitch.**—This is mainly used as pulverisable fuel, but it is not produced on a large scale in this country, chiefly because its manufacture involves excessive wear and tear on the distillation plant.

**2. Anthracene Oil.**—On cooling to atmospheric temperatures this oil deposits a mixture of crystals of anthracene, phenanthrene, and carbazole; these crystals are drained on a centrifuge and sold as the “40 per cent. anthracene paste” of commerce. The 40 per cent. paste can be worked up to 90 per cent. anthracene or more by fractional crystallation from pyridine, but this is not often practised to-day as it is more economical to synthesise anthraquinone from phthalic anhydride and benzene (see later). The clear oil separated from the anthracene paste is used in fluxing pitches to road-tar or in making special types of creosote.

**3. Creosote Oil.**—The total creosote produced by the tar distiller consists not only of the creosote fraction from the stills but also the washed and filtered middle oils and the filtered anthracene oil (see the flow diagram). About half the creosote available in Great Britain is hydrogenated to motor spirits at Billingham by the I.C.I., and the other half is used in wood preserving, as fluxing oils for the preparation of road tar, and in the manufacture of sheep dips, etc.

**4. Naphthalene Oil.**—Continuous stills equipped with a good fractionating column deliver a naphthalene oil which sets solid at ordinary temperatures. This solid is drained, broken up, and then gently warmed to give a slurry which is pumped to a hydraulic press. There the slurry, which consists of crystals of naphthalene suspended in light creosote oil, is subjected to a pressure of two tons per sq. in., and the oil which is expressed escapes through slits in the press liner and runs to storage. The naphthalene cakes expelled by the press ram are sold in this form as “hot-pressed naphthalene.” Alternatively the slurry is passed to a centrifuge where solid and liquid are separated. The naphthalene so obtained is the “crude whizzed naphthalene” of commerce.

Pure naphthalene is made by melting the hot-pressed cakes, washing with concentrated sulphuric acid, and then fractionally distilling the treated material. The distillate is further resublimed from a steam-heated pan into a large chamber, where the crystals collect on the floor and the walls. These crystals are “flake naphthalene” and have a melting-point of  $79.5^{\circ}$  C.



[Courtesy: The Wilton Patent Furnace Co. Ltd, Horsham.]

Fig. 191.—Boiling Ranges of Products obtained from a Continuous Tar Still.



5. **Carbolic Oil.**—This fraction is washed with caustic soda solution to give an aqueous extract of the phenolic bodies in the form of sodium phenates, and then washed with dilute sulphuric acid to remove the tar-bases as sulphates. The residual oil is light creosote and is either blended with the other creosotes or sold for special purposes. See paragraphs 10 and 11 (pp. 429–30) for the working up of the aqueous extracts.

6. **Light Oil.**—This is washed with caustic soda, and then with dilute sulphuric acid to remove phenols and tar bases respectively. The aqueous extracts are added to the corresponding washings of the carbolic oil, and the washed light oil then added to the crude benzole storage tank. The crude benzole is obtained from gasworks and coke oven plants by washing the gas with an oil, and subsequently steam distilling the oil to obtain the benzole from it. (See the chapter on the Gas Industry for the full details of this process.) The crude benzole so obtained, together with the light oil from the tar stills, is the raw material for the benzole refining plant (see paragraph 9 (below)).

7. **Road Tar.**—The British Road Tar Association's recommended method of preparing road tars involves the "cutting back" of a soft pitch. Crude tar is distilled to give a "base tar" of soft pitch having a viscosity slightly higher than that of any grade of road tar. This "base tar" is then fluxed with a suitable mixture of tar oils until the product is of the required viscosity and possesses the other characteristics demanded by the buyer's specification. Most road tar to-day is manufactured to meet the British Standard Specification No. BS. 76, 1943. Although a large quantity of tar is used in the manufacture of tar macadam and tar carpets, surface dressing of roads by spraying with tar and rolling in chippings is still a very important method of road maintainance. A surface dressing correctly applied should last at least three years under very heavy traffic.

8. **Coal-tar Fuels.**—These are prepared by fluxing pitch with creosote to give a black product known as pitch-creosote mixture. This fuel is extensively used in place of petroleum. The actual viscosity employed varies, and depends among other things on the temperature prevailing at the burner jets. The Association of Tar Distillers have produced a handbook entitled "Coal-tar Fuels" which gives full details of the use of these pitch-creosote mixtures.

9. **Benzole.**—Crude benzole is usually purchased by the tar distiller from neighbouring gasworks and coke ovens undertakings and, as described in paragraph 6 (above), it is mixed with the washed light oils from the tar stills before entering the benzole refinery. The layouts and methods of operation of benzole refineries vary considerably in this country, and the one given below is only one of the many possible arrangements. The flow of material through the plant is shown in Fig. 192.

The initial distillation takes in the Barbet column, which is a continuous fractionating unit operating at a high reflux ratio (up to 20 : 1). This gives an overhead distillate called "forerunnings," containing about 15–25 per cent. carbon disulphide, together with a mixture of light boiling hydrocarbons, which includes pentane, cyclopentadiene, hexane, etc. From the bottom of the column flows the CS<sub>2</sub>-free benzole, which normally contains less than 0.01 per cent. of CS<sub>2</sub>. This CS<sub>2</sub>-free benzole is then redistilled in a batch still equipped with a 12-plate column, and there separated into motor benzole and a residues fraction. The residues are steam distilled in another batch still to give a distillate, consisting principally of coumarone and indene, and a heavy residue which is returned to the crude tar storage tank. The coumarone-indene mixture is used in the manufacture of synthetic resins.

The motor benzole fraction from the first batch distillation consists essentially of benzene, toluene, and the xylenes, together with some unsaturated hydro-



carbons, and 0.5–1.0 per cent. of thiophen and its homologues. These sulphur compounds and the unsaturated hydrocarbons are removed by agitating the motor benzole with about 2 per cent. of its volume of 95 per cent. sulphuric acid in lead-lined vessels holding some 4,000 gallons. Resinification of the unsaturated hydrocarbons and the thiophens occurs and the resins dissolve in the acid to form an evil-smelling black liquid. This is run off through a valve in the bottom of the washing vessel, and the remaining benzole washed with aqueous caustic soda solution until neutral, and then with water to remove any suspended alkali droplets. The washed motor benzole is then fractionated in a continuous distillation unit of the type illustrated in Fig. 193.

This unit consists of three columns. The feed is put in near the central plate of the first column. An overhead fraction of pure benzene is taken off, and the residue from the bottom, consisting of toluene and its higher homologues, is passed to middle of the second column. Here an overhead fraction of pure toluene

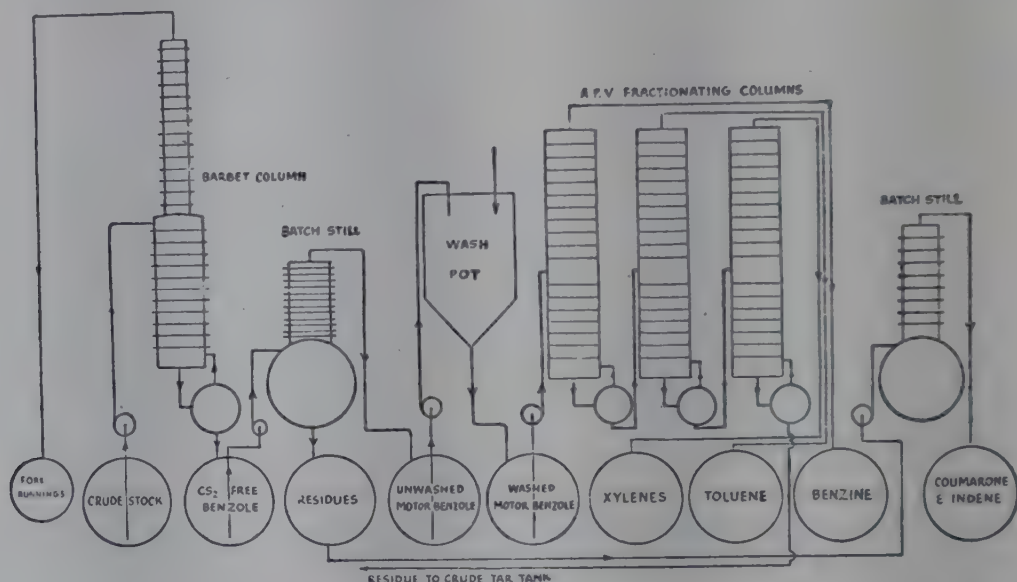


FIG. 192.—Flow Diagram of a Crude Benzol and Light Oil Rectification Plant.

is removed, and the residue passed to the third column where xylenes are taken off at the top. The residue from this third column is either steam distilled or passed back to the crude tar tanks.

An alternative procedure is often practised whereby the washed motor benzole is re-run in a simple batch still to give a colourless product consisting of benzene, toluene, and the xylenes. This mixture, which has an octane number of about 100, is sold to The National Benzole Company for enriching petroleum spirits. If the sulphur content of the unwashed motor benzole is less than 0.4 per cent. the washing with sulphuric acid can be omitted, and the unwashed spirit sold directly as motor benzole. In this case there are still unsaturated hydrocarbons present, and these can give rise to coloured gummy products by oxidation and polymerisation on storage. To overcome this difficulty the inhibitor process has been adopted. It consists of the addition to the spirit of a small quantity (about 0.05 per cent.) of orthocresol, catechol, or similar material, which acts as an anti-oxidant, and so slows down the rate of oxidation and polymerisation that the benzole is perfectly stable even on prolonged storage.

The forerunnings fraction from the Barbet column is agitated in a reaction tank with ammonium polysulphide solution. The carbon disulphide combines to give ammonium perthiocarbonate, which is soluble in the aqueous layer. This is drawn off and decomposed by steam to yield  $\text{CS}_2$  again and regenerate the ammonium polysulphide. The  $\text{CS}_2$ -free hydrocarbons are either mixed with the motor benzole or worked up for cyclopentadiene.



It is in the working up of the light oils and the benzole fraction that a real difference between gasworks' and coke ovens' crudes becomes apparent. Material from gasworks is always contaminated with traces of paraffinic and naphthenic hydrocarbons, which come mainly from the gas, but also from the paraffin wash oil used by these undertakings. Gas from vertical retorts has an even higher paraffin content than that from horizontals. On the other hand, coke oven gas



*Photo by courtesy]*

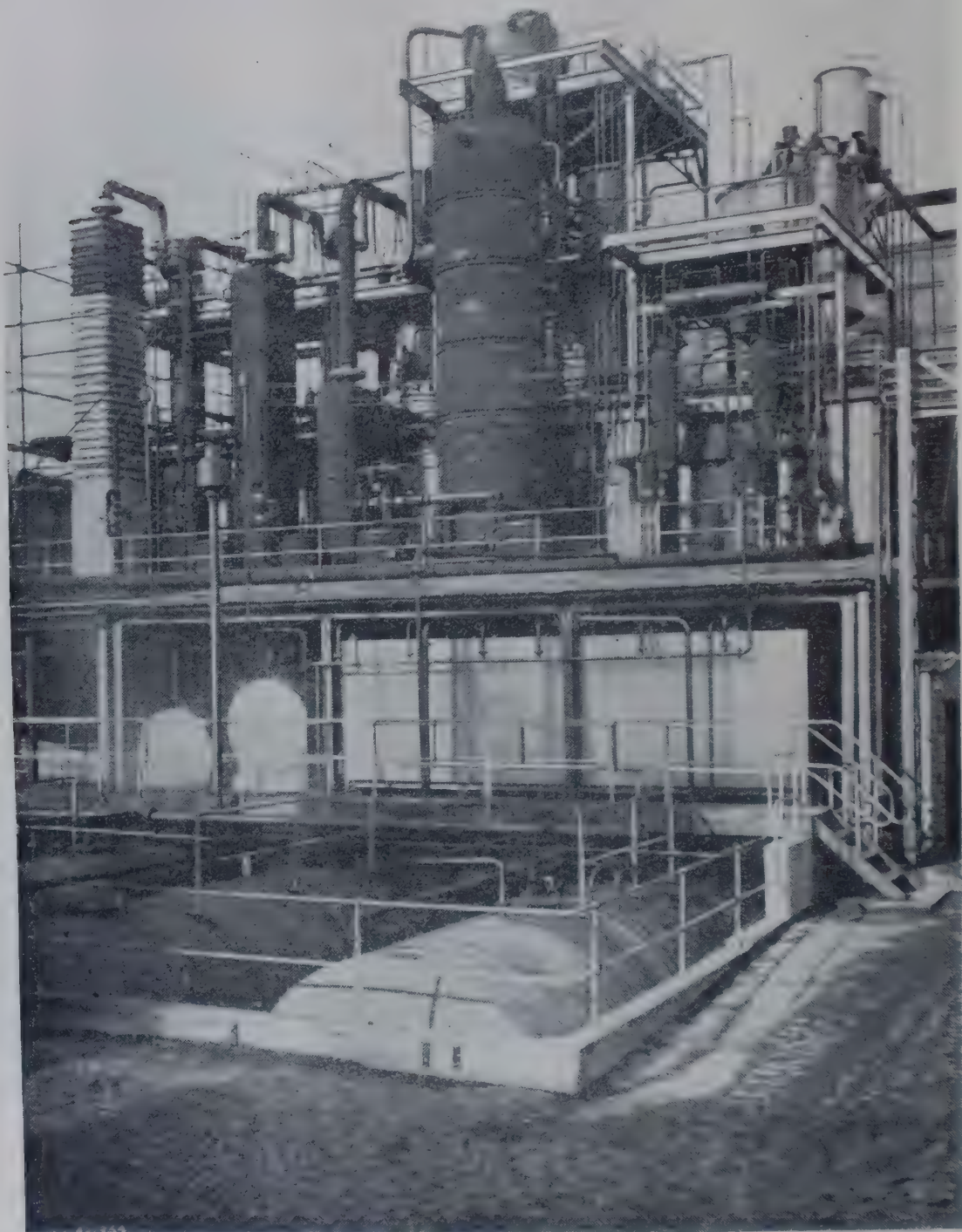
*[The A.P.V. Co. Ltd., London.*

FIG. 193.—Continuous Benzole Fractionating Unit, shown in course of construction.  
(Note the storage tanks in the background.)

contains only traces of paraffins, and there is little danger of contamination from the wash oil, because most of these concerns wash their gas with creosote and obtain an almost undiluted aromatic crude. These contaminating paraffin hydrocarbons form azeotropic mixtures with the aromatics, and cannot be removed by any ordinary distillation process, so that in normal times it may generally be said that only coke ovens' spirits are worked up to pure products, while gasworks' crudes are merely worked as far as the motor benzole stage and sold as such. During the 1939-45 war, however, the demand for toluene to be nitrated to T.N.T. was so great that toluene from all sources had to be used. The presence of traces of paraffin in toluene prepared from gasworks' crudes interfered with the process of nitration, and methods of removing the non-aromatic constituents



were sought. The method finally adopted was the "pseudo-azeotropic" process of the A.P.V. Co. Ltd., of London, and a large scale plant was erected. The principle involved is as follows. An acetone and methyl alcohol azeotrope is



*Photo by courtesy]*

*[The A.P.V. Co. Ltd., London.*

FIG. 194.—Plant for the separation of Aromatic from Non-aromatic Hydrocarbons by the Pseudo-Azeotropic Process.

fed to a continuous distillation column and distilled with the toluene-paraffin mixture. The head product is acetone and paraffin, while the base product is methyl alcohol and toluene. In this way over 2,500 gallons of high gravity nitration quality toluene were recovered per day from low gravity fractions obtained from gasworks' crudes, and this with an enhanced yield but no increase in steam consumption, as compared with the orthodox methods for low gravity crudes.



The mechanism of this process is of considerable theoretical interest as well as practical application. When separation is achieved in the presence of added "entraining agents," the mechanism almost invariably involves the formation of constant boiling mixtures between the entrainer and components of the mixture (for example, in the manufacture of 99.9 per cent. alcohol from aqueous spirits by distillation in the presence of benzene). Investigation shows that in the A.P.V. process no such constant boiling mixture is formed, although the sharpness of separation is considerably greater than can be obtained using azeotropic entrainers in the ordinary way. The plant constructed in the recent war is illustrated in Fig. 194.

**10. Tar Acids (Phenols).**—From the fractions containing them these are extracted as an aqueous solution of the sodium salts of the phenols. This solution is termed "carbolate," and contains traces of tar bases in solution and of neutral oils in suspension. To remove these impurities the solution is boiled in an evaporator. The bases and neutral oils distil off, are condensed, and are returned to the crude tar, while the phenols remain in solution, being non-volatile in the

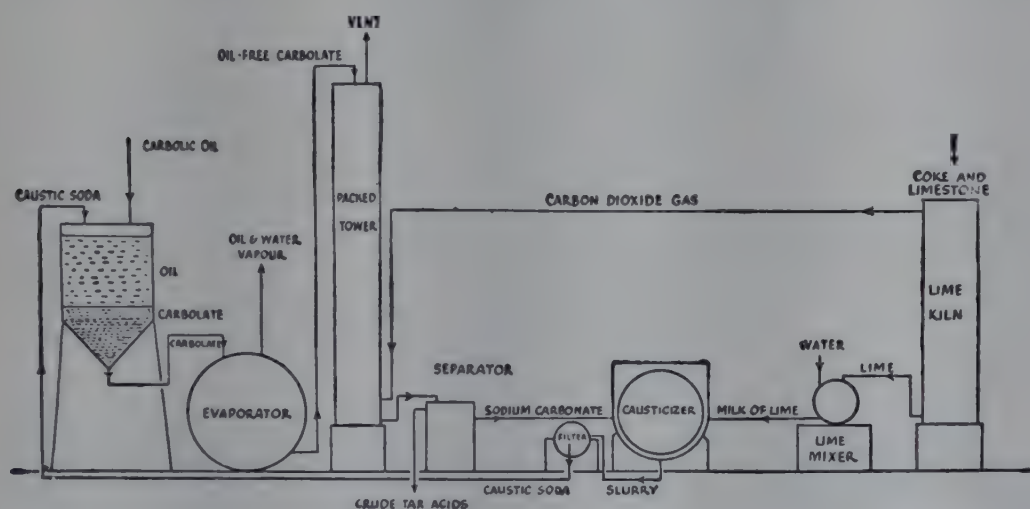


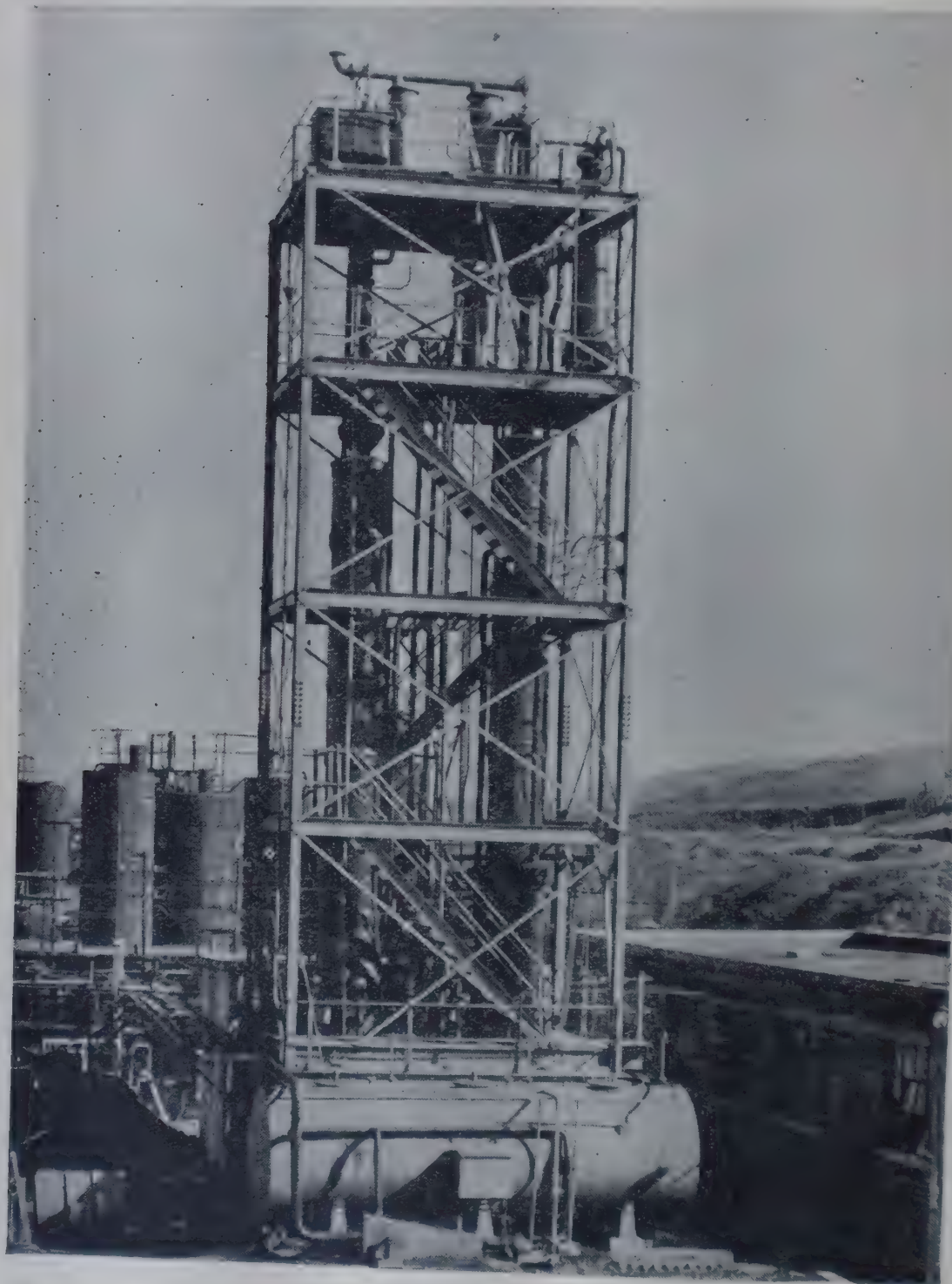
FIG. 195.—Diagrammatic Layout of Crude Tar Acids Extraction Plant.

form of their sodium salts. From the evaporator the carbolate is pumped to the top of a packed tower and let trickle down against an upward current of carbon dioxide gas (see Fig. 195). This carbon dioxide, which is obtained from a lime kiln, decomposes the carbolate into two immiscible liquids—crude tar acids and sodium carbonate solution. These are separated by an orthodox gravity separator, whence the tar acids flow to the crude phenols storage tank and the sodium carbonate solution to a causticiser. Here lime from the kiln is added in order to convert the carbonate to caustic soda. The chalk which is precipitated is filtered off on a continuous rotary filter and discarded, while the caustic soda solution formed goes back to the stock tank for washing more carbolic oil.

The tar acids are fractionally distilled under vacuum in a continuous unit similar to that illustrated in Fig. 196. The number of columns employed depends on the number of fractions required, and the use of a vacuum distillation unit both reduces the steam consumption of the plant and avoids charring the crude phenols. The fractions which the distiller may have to produce are phenol, *o*-cresol, *m*- and *p*-cresols, the xylenols and high boiling tar acids; a typical plant comprising seven columns, as shown in Fig. 197, would be required to make these. The first column is merely a dehydrator, the second is to remove pitchy and resinous material as a base product and to give a distillate of dry crude phenols. Each of the five remaining columns has a heads fraction corresponding to one of the five fractions required.



**II. Tar Bases.**—These are heterocyclic nitrogen compounds and are extracted from the light and middle oils by dilute sulphuric acid as an aqueous solution of the sulphates of pyridine, the picolines, lutidines, quinolines, etc. The bases are liberated from the sulphate solution by passing in dry ammonia



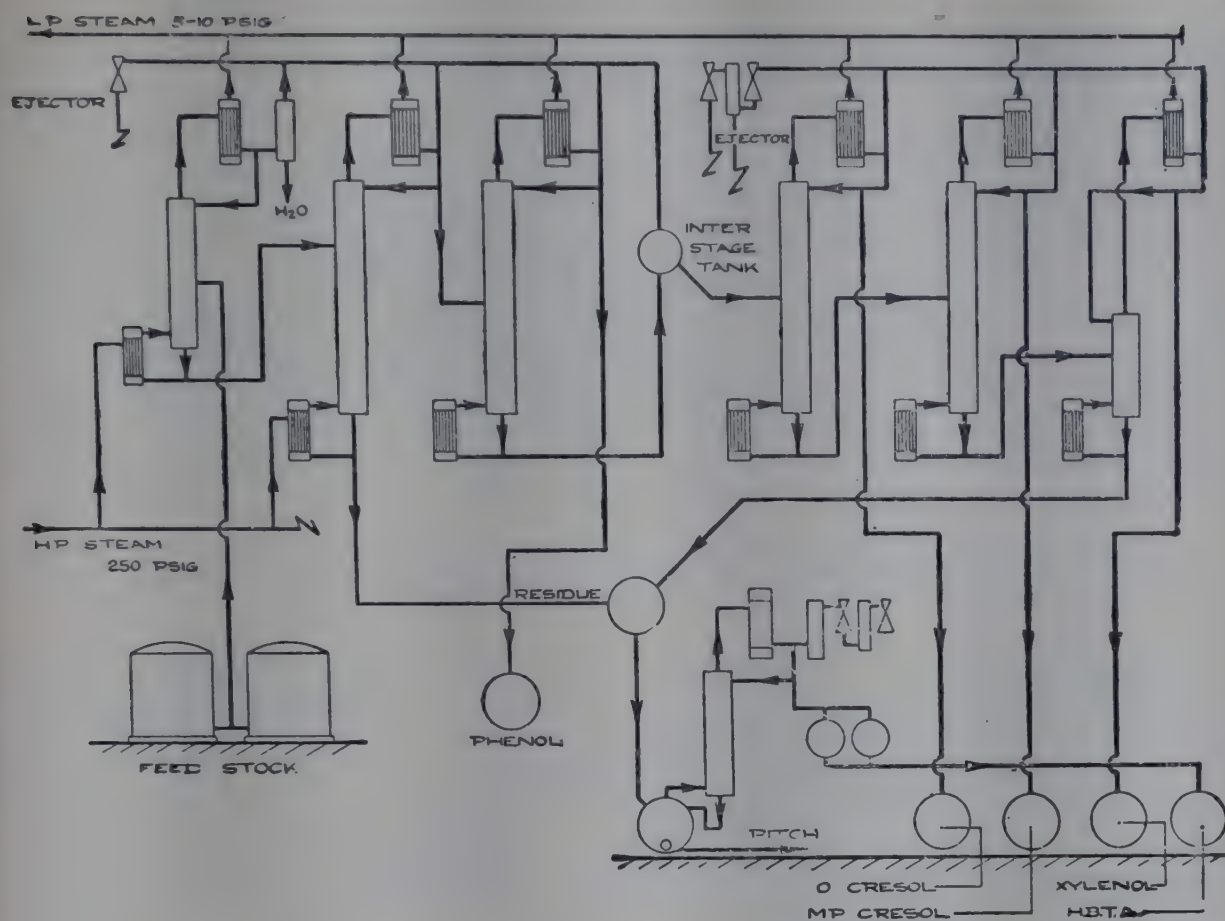
*Photo by courtesy]*

*[The A.P.V. Co. Ltd., London.*

FIG. 196.—Continuous Distillation Unit for separating pure phenol and *o*-cresol from *m*- and *p*-cresols, etc.

gas or by the addition of solid caustic soda. Being insoluble in the strongly alkaline solution of sodium or ammonium salts the bases float on the aqueous layer and are separated by gravity in the usual manner. Dehydration of the mixed bases is effected by solid caustic soda, and separation is a matter of fractional distillation. The lighter boiling tar bases are very soluble in water and are hygroscopic, so that undue exposure to the atmosphere must be avoided in transport and storage.





[By courtesy: The A.P.V. Co. Ltd., London.]

FIG. 197.—Preparation of Pure Phenols from Crude Tar Acids (flow diagram).

### The Testing of Coal-tar Products

Testing procedure for coal-tar and coal-tar products has been rigidly standardised in this country by the Standardisation of Tar Products Tests Committee, whose handbook "The Testing of Coal-tar and its Products" is revised every few years. Specifications to which products should conform are published by the British Standards Institution.

### The Properties and Uses of Pure Coal-tar Products

1. **Carbon Disulphide,  $\text{CS}_2$ .** M.P.  $-111.8^\circ \text{C.}$ ; B.P.  $46.3^\circ \text{C.}$ ; S.G. 1.262 (20/4).—This evil-smelling liquid occurs to the extent of about 20 per cent. in the forerunnings of benzole distillation. It is principally used for extracting natural oils and fats from seeds and in the vulcanisation of rubber.

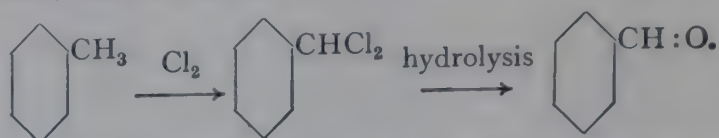
2. **Cyclopentadiene,  $\text{CH}_2$**   $\begin{array}{c} \text{CH}=\text{CH} \\ | \\ \text{CH}=\text{CH} \end{array}$ . B.P.  $42.5^\circ \text{C.}$ ; S.G. 0.805 (19/4).—

This also occurs in forerunnings. It rapidly polymerises to the dimeric form.

3. **Benzene,  $\text{C}_6\text{H}_6$ .** M.P.  $5.6^\circ \text{C.}$ ; B.P.  $80.1^\circ \text{C.}$ ; S.G. 0.872 (25/4).—Benzene is a colourless, mobile liquid. Apart from its use as a constituent of motor fuels it finds application in the manufacture of dyestuffs intermediates. Nitrobenzene and aniline are typical derivatives of benzene in this connection. Benzene is also the starting material for the preparation of chlorobenzene, synthetic phenol, D.D.T., gammexane, and nylon (see section on Coal Tar Derivatives).

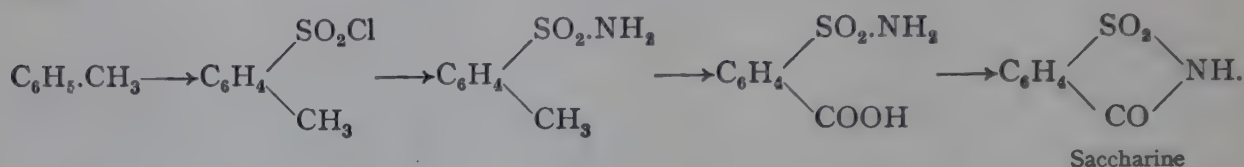
4. **Toluene,  $\text{C}_6\text{H}_5\text{CH}_3$  (methyl benzene).** M.P.  $-95.0^\circ \text{C.}$ ; B.P.  $110.6^\circ \text{C.}$ ; S.G. 0.862 (25/4).—Has similar chemical properties to benzene, and is the raw

(b) *Benzaldehyde*,  $C_6H_5CH : O$ , and *Benzoic Acid*,  $C_6H_5COOH$ .—These are prepared from toluene, via benzal chloride, thus:

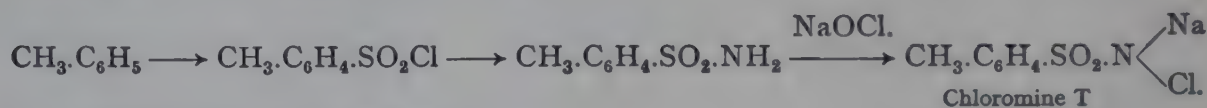


Benzaldehyde is used in perfumery and its sulphonic acids form the parent substances of dyes. Benzoic acid is a mordant for calico printing and enters into the preparation of aniline blue.

(c) *Saccharine and Chloramine T*.—Toluene reacts with chlorosulphonic acid to give a mixture of *o*- and *p*-toluene sulphonyl chlorides, the latter being the chief product. The ortho-compound is converted into the corresponding sulphonamide and the methyl group then oxidised with alkaline permanganate. On acidification one molecule of water is lost, and saccharine crystallises out thus:



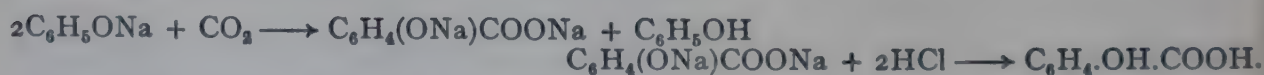
The para-toluene sulphonyl chloride, which is also formed in the first stage, is converted into chloramine T, thus:



### 3. Derivatives of Phenol.

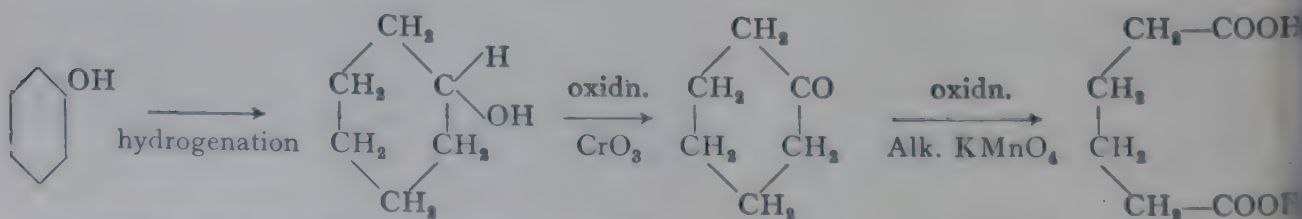
(a) *Picric Acid*,  $C_6H_2\text{OH}(\text{NO}_2)_3$ .—This is prepared by nitration of phenol sulphonic acid, the direct nitration of phenol being too violent a reaction. It is used as a dye directly, also in the tanning industry, and in explosives.

(b) *Salicylic Acid*,  $C_6H_4\text{OH}\text{COOH}$ .—Dry sodium phenate reacts with dry carbon dioxide, yielding a disodium salt of salicylic acid. Hydrolysis with hydrochloric acid results in the free acid being precipitated. The reactions involved are:



The phenol formed in the first stage must be distilled off as fast as it is formed in order to obtain a reasonable yield of salicylic acid. Salicylic acid is used in food preservation, medicines, and in the production of azo-dyes.

(c) *Adipic Acid*,  $(\text{CH}_2)_4 \begin{array}{l} \text{COOH} \\ \text{COOH} \end{array}$ , is prepared from phenol, via cyclohexanol and cyclohexanone, as under:



Adipic acid is of value as the parent substance of the nylon type of plastics.

### 4. Derivatives of Naphthalene.

(a) *Naphthols*.  $\alpha$ - and  $\beta$ -naphthols are prepared from the corresponding naphthalene sulphonic acids by fusion with caustic soda. They are important dyestuffs intermediates.

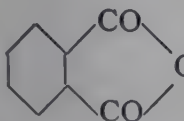


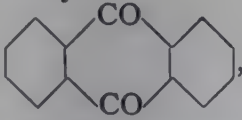
(b) *Chloronaphthalenes*.—These are produced by chlorination of naphthalene, and are the basis of the "Seekay" waxes, which are said to have flame- and waterproof properties.

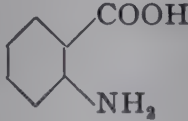
(c) *Nitronaphthalenes*.—The  $\alpha$ -compound is made by nitrating the naphthalene with a sulphuric and nitric acid mixture at  $45^{\circ}$ – $60^{\circ}$  C. The  $\beta$ -compound is difficult to prepare industrially.  $\alpha$ -nitronaphthalene is used in the manufacture of dyes and to a limited extent in explosives.

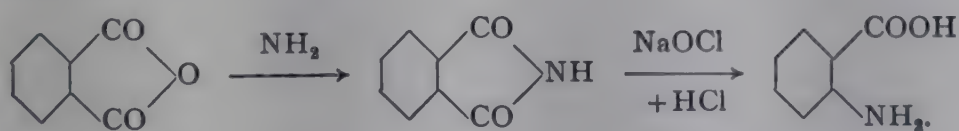
(d) *Naphthylamines*.—The  $\alpha$ -compound is prepared by reducing the corresponding nitronaphthalene with iron borings and hydrochloric acid, as in the manufacture of aniline.  $\beta$ -naphthylamine is the product of reacting  $\beta$ -naphthol, ammonium sulphite, and ammonia in an autoclave at  $100^{\circ}$ – $150^{\circ}$  C. for 8 hours. Both the naphthylamines are important intermediate compounds in dye manufacture.

(e) *Decalin* and *Tetralin*.—Hydrogenation of naphthalene produces both decahydronaphthalene (decalin) and tetrahydronaphthalene (tetralin). Their uses include substitutes for turpentine, solvents, crystallising media, and to a limited extent motor fuels.

(f) *Phthalic Anhydride*, , is prepared by oxidising naphthalene with air in the presence of a catalyst. It is used directly in the preparation of dyes, photographic chemicals, and in the manufacture of anthraquinone (see below). It reacts with glycerine, forming the "glyptals" or alkyd-resins which have film forming properties, and so find extensive use in the paint, varnish and lacquer industry.

(g) *Anthraquinone*, , is usually made by the reaction of benzene and phthalic anhydride in the presence of aluminium chloride at  $70^{\circ}$  C. An alternative method by oxidising anthracene used to be used, but has practically been abandoned to-day. It is used in the manufacture of alizarin, quinizarine, and purpurine.

(h) *Anthranilic Acid* (*o*-amino-benzoic acid), .—This is prepared from phthalic anhydride as under:



It is the starting material for the manufacture of synthetic indigo.

In conclusion, the author wishes to thank the following firms for their generous assistance in compiling this section, and for loans and gifts of blocks and photographs:—

The A.P.V. Co. Ltd., London.

The Chemical Engineering and Wilton's Patent Furnace Co. Ltd., Horsham.





## SECTION XIII

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### Industry of the Synthetic Colouring Matters





# INDUSTRY OF THE SYNTHETIC COLOURING MATTERS

Originally written by THOMAS BEACALL, B.A.(Camb.),  
and G. MARTIN, Ph.D., D.Sc.  
Revised by E. I. COOKE, M.A.(Cantab.), B.Sc., A.R.I.C.

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## INTRODUCTION

THE origin and development of the coal-tar dye industry represents one of the greatest triumphs of modern chemistry.

In 1834 Runge discovered phenol and aniline in coal-tar. The researches of A. W. Hofmann (1842-63) revealed the chemical nature of several of the more important constituents of coal-tar. The industry practically dates from 1856, when Perkin obtained **Mauve** by oxidising aniline. In 1859 Verguin isolated **Fuchsine**. Soon afterwards **Aniline Blue** was discovered, which Hofmann in 1863 showed to be a derivative of Rosaniline. In 1868 and in 1869 Graebe and Liebermann synthesised **Alizarin** from anthracene by two methods, the second of these being almost simultaneously discovered by Perkin. In 1871 Baeyer discovered the **Phthaleins**. In 1876 E. and O. Fischer worked out the constitution of the **Rosaniline colours**. About the same time the manufacture of the **Azo colours** was begun. In 1884 the **Congo Red Cotton Dyes** were introduced. **Indigo** was synthesised by Baeyer in 1880, but its manufacture only became a commercial success after Heumann's synthesis in 1890, the product being placed on the market by the Badische Anilin- und Soda-Fabrik in 1897. The first sulphur dye, **Cachou de Laval**, was made by Croissant and Bretonnière in 1873, but the sulphide dye manufacture dates practically from **Vidal Black** (1893). In recent years the most noteworthy dates are 1901, the year of the discovery of the first **Anthracene Vat Dyes** by the Badische Anilin- und Soda-Fabrik, and 1905, when **Thioindigo** was produced by Friedländer.

Although the dye industry was founded in England by Perkin, who established a factory for the manufacture of Mauve, and later of Alizarin, the trade then passed largely into German hands. This has been attributed to a variety of causes which cannot be considered at length here. Suffice it to say that probably one of the most weighty of these causes was the unfortunate divorce of science from industry which largely prevailed in this country until recently, whereas the contrary was the case in Germany. It is noteworthy that the men who founded and built up the enormous German undertakings were not business men in the usual sense of the word, but were themselves chemists of note and realised to the full the importance of research. Then, too, every improvement was patented, and the industry was thus gradually surrounded by a ring of patents, which rendered the entry of new competitors into the market increasingly difficult. Among the German colour factories the following may be especially noted: The Badische Anilin- und Soda-Fabrik in Ludwigshafen am Rhein is one of the largest chemical factories in the world, employing 7,500 workmen, 197 university trained chemists, 95 engineers, and 709 clerks (1906). The Farbenfabriken vormals F. Bayer & Co. in Elberfeld and Leverkusen is almost as large. Other very large firms are Cassella & Co., in Frankfurt am Main, the Farbwerke vormals Meister Lucius & Brüning of Höchst, the Aktiengesellschaft für Anilin Fabrikation of Berlin, and Kalle & Co. of Biebrich. The most important British firms are Messrs Cole & Wilson, Colne Vale Dye and Chemical Co., H. F. Robinson, M. W. Hardy, Broom & Forth, Garthwood, Bernard Keegan, LPC Chemicals & Dyes, H. M. Roermole, Bryce Roberts.

**Statistics.**—The following numbers show the value of the import of synthetic dyes into the United Kingdom (almost entirely from Germany):—

## IMPORTS

	1906.	1913.	Value in 1913.
	Cwt.	Cwt.	
Alizarin and anthracene dye-stuffs . . .	57,300	60,800	£272,000
Aniline and naphthalene dye-stuffs . . .	188,600	283,000	1,543,000
Synthetic indigo . . . . .	39,000	23,900	76,700
Other coal-tar dye-stuffs . . . . .	700	155	570,000
<b>Total . . . . .</b>	<b>285,600</b>	<b>367,855</b>	<b>£2,461,700</b>

The United States *imported*, principally from Germany:—

	1906.	1910.	Value in 1910.
	Lbs.	Lbs.	
Alizarin colours . . . . .	3,882,000	3,023,000	\$648,000
Coal-tar colours and dyes . . . . .	...	...	6,011,000
Indigo . . . . .	7,393,000	7,540,000	1,196,000

The United States exported of dyes and dyestuffs—\$491,000 in 1906, and \$380,000 in 1910. The German net export of coal-tar colours (including aniline oils and intermediate products) amounted in 1909 to 1,600,000 cwt. (more exactly, 83,250 metric tons), having a net value of £10,000,000.

For statistics regarding **Indigo** see p. 461.

For modern statistics see Appendix III.

Almost all the artificial colouring matters are derivatives of benzene, naphthalene, or anthracene, which are obtained from coal-tar. 1,000 tons of coal-tar yield, when worked up, 2.5 tons of fuchsine, 0.75 ton of indigo, 0.2 ton of alizarin, and 0.2 ton of picric acid. Since the number of artificial dyestuffs runs into several thousands, it is impossible within the limits of the present article to mention more than a few of the more important of each separate group, placing special emphasis on new classes of dyestuffs, such as have been specially developed within the last few years. For particulars of special dyes the reader must consult the works cited at the beginning of this section.



**The Theory of Colour in Dyestuffs.**—It has been found that the degree of chemical unsaturation in a compound controls the selective light absorption of that compound. Substances containing double or triple bonds have the property of being able to absorb light of certain wave-lengths. Selective absorption:

Groups which show such absorption are  $\text{>C=C<}$ ,  $\text{—N=N—}$ ,  $\text{>C=S}$ ,  $\text{—C}\equiv\text{C—}$ ,  $\text{—N}\begin{smallmatrix} \text{O} \\ \text{<} \end{smallmatrix} \begin{smallmatrix} \text{O} \\ \text{>} \end{smallmatrix} \text{—}$ ,  $\text{—N=O}$ ,  $\text{—C}\begin{smallmatrix} \text{O} \\ \text{<} \end{smallmatrix} \begin{smallmatrix} \text{O} \\ \text{>} \end{smallmatrix} \text{OH}$ ,  $\text{>C=O}$ . Selective absorption by groups such as the above gives rise to colour when the absorption wave-length lies within certain values.

Atoms or groups of atoms giving rise to absorption of light are called chromophoric groups or chromophores. It has been found experimentally that these groups are usually unsaturated. Co-ordinate unsaturated atoms in a molecule give rise to light absorption. The latter is increased when the co-ordinate unsaturated atoms are changed to the ionic state. The intense colour of triphenylmethane dyes is an example of this change.

Modern atomic theory explains chromophores in the unstable arrangement of electrons. In chromophores the atoms contain electrons which have been transferred to quantum states of greater energy by the absorption of light energy. This means that almost all atoms and ions, except the hydrogen ion, are capable of light absorption, and this is indeed the case, but in a large number of cases the subsequent "colour" is outside the visible range, *i.e.*, in the short wave ultra-violet.

It is not unnatural that we find the electronic structure of radicals and ions distorted in which electrons are missing. These radicals have an electron number less than the total nuclear charge. As mentioned above, the triphenylmethane dyes are an example of this state of affairs.

Colour is dependent upon constitution and not composition. We may have compounds of the same empirical chemical composition and yet with totally different chemical constitution and colour. For example, the compound  $\text{CH}_3\text{CO.CO.CH}_2\text{.CH}_3$  has a pronounced yellow colour which is common with compounds in which the carboxyl groups are adjacent. The compound,  $\text{CH}_3\text{.CO.CH}_2\text{.CO.CH}_3$  is colourless, although it has the same chemical composition as the first one.

Several attempts have been made to establish a connection between chemical constitution and colour, but there has been very little success except with very closely related compounds.

When an aromatic compound, such as toluene, say, undergoes substitution or other chemical change, its colour may deepen or lighten. When the colour deepens the group causing the deepening is called a bathochrome group. Similarly when the group inserted causes a lightening of the coloured compound it is called a hypsochrome group.

There is another class of chemical group called the auxochrome. Auxochromes are acid or basic groups of the type  $\text{—NH}_2$ ,  $\text{—COOH}$ ,  $\text{—SO}_2\text{.OH}$ ,  $\text{—OH}$ . Their action in dyestuffs is to intensify the colour and to provide an active group by means of which the dyestuff can attach itself on to the fabric. Auxochromes may also act as bathochrome or hypsochrome groups.

The vast majority of dyes are organic. Indeed, it can probably be said that all the useful dyes are organic chemicals.

A fabric to be dyed generally belongs to one of three classes: vegetable fibres, such as cotton, hemp, flax or jute, which are chemically composed of approximately neutral cellulose; animal fibres, such as wool, silk and leather, which consist chemically of proteins, amphoteric in nature and therefore capable of combining with both acid and basic dyestuffs; synthetic fibres, such as regenerated cellulose, cellulose acetate, nylon, terylene and saran, which, with the exception of the first, often require special treatment during dyeing.



The choice of dye and the method of dyeing is determined by the nature of the textile fibre. For example, wool and silk which have an amphoteric structure are dyed readily by both acidic and basic dyes. On the other hand, vegetable fibres, such as cotton, are less receptive and it is necessary to use colloidal suspensions of special dyes—substantive or direct dyes. Cotton may be dyed with other dyes, however, if a mordant (see below) has been used in conjunction with the dye.

Two types of mordants (to "bite," *i.e.*, to fix the dye) are generally recognised; acidic and basic or metallic. When an acid mordant is used, the cloth to be dyed is steeped in a solution of the acid (*e.g.*, tannic acid). This is absorbed in the fibres. When a basic dye is used with this mordanted cloth, the basic groups of the dye react with the acidic groups of the tannic acid, after which the whole complex is firmly fastened to the cloth.

When a basic (or metallic) mordant is used, the cloth is steeped in a solution of a readily hydrolysed metallic salt. The metal is usually chosen from the trivalent series: aluminium, ferric iron, or chromium. Stannous salts are also used. Acetates and alums are generally used in the case of chromium. The steeped cloth is then placed in superheated steam which causes the salt to hydrolyse, precipitating a colloidal basic salt complex in the fibre. This mordanted fabric is then placed in a solution of a dye capable of combining with the basic salt. A complex compound called a lake is then formed in the fibre. The dye is thus fixed in the fibre by chemical combination with the basic salt which has already been precipitated within the fibre. The above dye is then said to be fast. An acid dye (see below) is required for use with a basic salt mordant.

When cotton is mordanted with tannic acid the latter is absorbed in the thread and then reacts chemically with basic dyes (see below), thus fixing them.

There has been considerable research into the mechanism of dyeing. A prominent name in this connection is Witt. He maintained that the dye formed a solution with the fibre, distributing itself between the latter and the water according to Henry's Law, as when two immiscible liquids are in contact. Kartarchoff and K. H. Meyer think that certain cellulose acetate and nitrate dyes are attached in this way.

In other cases, absorption by the fibre seems to take place. Substantive dyes on cotton are controlled by the absorption isotherm. In the case of wool, although there are many conflicting opinions, it seems that the most convincing explanation is simple salt formation between the basic part of the amphoteric wool molecule and the acidic part of the dye or the acidic part of the amphoteric wool molecule and the basic part of the dye, depending whether a basic or acidic dye is used.

K. H. Meyer has more recently investigated the combination of organic acids and acid dyes with silk and wool. He found that the weights of dye fixed in silk and wool were proportional to the equivalent weights of the silk and wool and were completely independent of the chemical nature of the dye. This supports the theory that the dyeing of silk and wool is a simple process of salt formation.

Recent theories of absorption are that the latter is due to excess valency forces in the atomic lattice. Consequently the differences between absorption and chemical union became less obvious and the drawing of a distinction between the two processes seems inadvisable.

**Classification of Dyes.**—Dyes may be classified either according to their chemical composition or according to their dyeing properties. In discussing the manufacture of dyes, the former method of procedure is the only suitable one, the second method being used when the technology of dyeing is under consideration.



The following scheme shows the arrangement followed in the present article, the three groups which are of the greatest importance at the present time being considered first :—

1. Azo dyes (including pyrazolone and stilbene dyes).
2. Dyes of the anthracene series.
3. Dyes of the indigo and thioindigo series.
4. Di- and tri-arylmethane dyes.
5. Pyrone dyes.
6. Azine dyes.
7. Oxazine dyes.
8. Dyes containing sulphur (thiazine, thiazole, and sulphide dyes).
9. Acridine dyes.
10. Minor groups of dyes—nitro and nitroso dyes, quinoline dyes, oxyketone dyes, indophenols, indamines, aniline black.

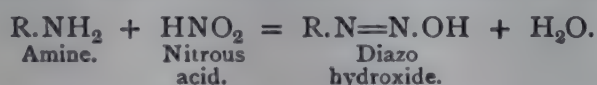
We will take them in this order in the following pages.

## I. AZO DYES

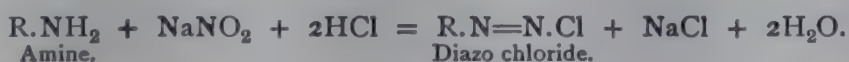
The azo dyes form the largest group of dyes known; they derive the name from their characteristic **azo** group, consisting of two nitrogen atoms and usually written  $\text{—N=N—}$ , or  $\text{—N}_2\text{—}$ . According as the azo group occurs one, two, three, four, etc., times in the molecule, the dyes are described as monoazo, disazo, trisazo, tetrakisazo, etc.

The azo dyes were discovered by Griess in 1858 and some were put on the market soon afterwards, but as a class the dyes did not come into existence until about 1876.

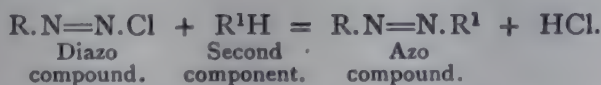
**Method of Preparation.**—When a primary amine is treated with nitrous acid at a low temperature, diazo compounds are formed according to the equation :—



In practice aromatic amines only are used, and nitrous acid is replaced by sodium nitrite and an acid, usually hydrochloric acid. The reaction then becomes :—



The diazo compounds can then react with other compounds, usually aromatic amines or phenols, producing azo compounds, which, if of suitable constitution, act as dyes. The reaction is :—



The amine which is diazotised is referred to as the diazo or first component, while the compound  $\text{R}^1\text{H}$  is called the second component.

The operation is carried out in practice as follows :—

A molecular proportion of the amine to be diazotised is dissolved in water with about  $2\frac{1}{2}$  molecular parts of hydrochloric acid; a solution of a molecular part of nitrite is then run in gradually while the reaction mixture is kept cool and stirred. After diazotisation is complete, the solution is added to a solution of a molecular proportion of the second component, and stirring is continued until the combination is finished; the dye either precipitates or is salted out by means of salt or hydrochloric acid, and is filtered off, washed and dried.

The diazo reaction is capable of very wide application, but some amines cannot be diazotised except under special conditions, while others do not give the normal diazo salts—some of these will be noted later. The diazo compounds in general are not very stable, accordingly some amines (aniline, toluidines, etc.) must be



diazotised at  $0^{\circ}\text{C}$ ., while for others (nitranilines, naphthylamines, etc.) a temperature of about  $10^{\circ}\text{C}$ . is suitable. In some cases (e.g., trinitraniline) the diazotisation is effected by nitrite in the presence of cold concentrated sulphuric acid, while the 1:2- and 2:1-aminonaphthols are diazotised in the presence of salts of copper, zinc, etc.

Besides nitrite, various other diazotising agents are occasionally employed, for instance, nitrosyl chloride, and nitrosulphonic acid.

It is unnecessary here to consider further the nature of the diazo compounds, or the various formulæ which have been proposed for them. A full discussion of these will be found in Cain's "Chemistry of the Diazo Compounds" (Arnold, 1908). Kekulé's formula,  $\text{R.N}=\text{N.X}$ , expresses the facts sufficiently for our present purpose.

In connection with the operation of coupling the diazo compounds with the second component, the following points should be noted: phenols are coupled in an alkaline solution (sodium carbonate), while if the second component is an amine it is coupled in a neutral or acid (usually hydrochloric or acetic) solution.

The azo group generally enters the molecule of the second component in the para-position to the amino or hydroxyl group of this body, or, if this combination be impossible, in the ortho-position. Thus aniline, phenol,  $\alpha$ -naphthol,  $\alpha$ -naphthylamine couple in the para-position,  $p$ -toluidine and  $p$ -cresol in the ortho-position, while  $\beta$ -naphthol couples in the  $\alpha$ -ortho-position. In the case of the naphthylamine or naphthol sulphonic acids, the positions of the sulphonic groups often determine the position taken up by the azo group. In the case of some of the heteronuclear aminonaphthol sulphonic acids, e.g., the 2:8:6, 2:5:7, 1:8:4, 1:8:5, 1:8:3:6 acids, different products are obtained according as the combination is effected in alkaline or in acid solution—in alkaline solution the azo group enters in ortho-position to the hydroxyl group, while in hydrochloric acid solution it enters in ortho-position to the amino group.

An important variation in the process of preparing azo dyes is the production of these dyes "on the fibre." A typical instance is **Paranitraniline red**; to produce this dye, the material to be dyed is impregnated with  $\beta$ -naphthol by passage through an alkaline bath of this compound, and is then passed into a second bath containing diazotised  $p$ -nitraniline, the dye thus being produced on the material. For use in this process the diazotised  $p$ -nitraniline is sometimes converted by the action of caustic alkali into a stable isomeric form, the so-called nitrosamine, which may be formulated  $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{NNa}\cdot\text{NO}$ , and is sold as such; when required for use, the nitrosamine is reconverted into the active diazo compound by treatment with acid (see pp. 450, 478, 545, 558).

### Monoazo Dyes, $\text{R.N}=\text{N.R}^1$

The monoazo dyes are prepared according to the methods described above; their number is very great, and only a few typical ones are described here. Their dyeing properties vary according to their constitution; a large number dye wool in acid baths; an important and growing group of these consists of the so-called ortho-oxyazo dyes, obtained from diazotised  $\alpha$ -aminophenolic compounds—these dye wool with chrome mordants; a large number of monoazo dyes are used as parent materials for the manufacture of pigments or lakes. Some typical monoazo dyes are tabulated below:—

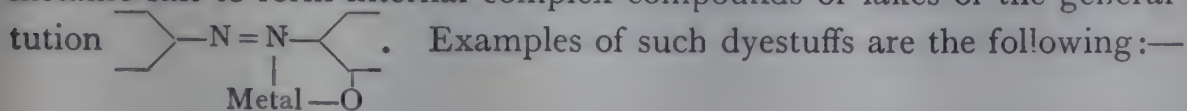
#### Acid Wool Dyes

Acid yellow	-	-	-	-	Aminoazobenzene disulphonic acid.
Azococcine 2R	-	-	-	-	Xylidine + 1:4-naphthol sulphonic acid.
Crystal Ponceau	}	-	-	-	$\alpha$ -Naphthylamine + 2:6:8-naphthol disulphonic acid.
„ scarlet 6R		-	-	-	
Fast red A	-	-	-	-	Naphthionic acid + $\beta$ -naphthol.
„ „ B	-	-	-	-	$\alpha$ -Naphthylamine + 2:3:6-naphthol disulphonic acid.
Lanacyl blue BR	-	-	-	-	1:8:3:6-aminonaphthol disulphonic acid + 1:5-aminonaphthol.
Metanil yellow	-	-	-	-	Metanilic acid + diphenylamine.
Orange II	-	-	-	-	Sulphanilic acid + $\beta$ -naphthol.
Palatine red	-	-	-	-	$\alpha$ -Naphthylamine + 1:3:6-naphthol disulphonic acid.
Ponceau 2G	-	-	-	-	Aniline + 2:3:6-naphthol disulphonic acid.
„ 2R	-	-	-	-	$m$ -Xylidine + 2:3:6-naphthol disulphonic acid.
„ 4R	-	-	-	-	$\psi$ -Cumidine + 2:3:6-naphthol disulphonic acid.
„ 6R	-	-	-	-	Naphthionic acid + $\beta$ -naphthol trisulphonic acid.
Tropaeoline O	-	-	-	-	Sulphanilic acid + resorcin.



## Dyes for Chrome-Mordanted Wool

(a) **From Diazotised *o*-Aminophenols.**—In order that a dye should be fixed by a metallic mordant it must possess the means of combining with a metallic salt to form internal complex compounds or lakes of the general constitution



4-acetylamino-2-aminophenol-5-sulphonic acid +  $\beta$ -naphthol, etc. (Cassella, English Patent, 3,182, 1903).

1-amino-2-naphthol sulphonic acids + naphthols, naphthol sulphonic acids, aminonaphthols, aminonaphthol sulphonic acids, dioxynaphthalenes, dioxynaphthalene sulphonic acids, resorcin, *m*-aminophenol, *m*-diamines, etc. (Geigy, English Patent, 15,025, 1904).

*o*-aminophenol and its methyl, chlor, nitro, etc., derivatives + chromotropic acid (M.L.B., English Patent, 26,383, 1905).

Nitro or chlor derivatives of *o*-aminophenol + 2-arylamino-5-naphthol-7-sulphonic acids (Bayer, English Patent, 14,921, 1906).

Nitro or chlor derivatives of *o*-aminophenol + alkyl or aryl derivatives of *m*-aminophenol (Bayer, English Patent, 25,177, 1908).

## (b) Other Dyes for Chrome-Mordanted Wool.—

Alizarine yellow GG	-	-	<i>m</i> -Nitraniline + salicylic acid.
Azochromine	-	-	<i>p</i> -Aminophenol + pyrogallol.
Azofuchsine B	-	-	Toluidine + 1 : 8 : 4-dioxynaphthalene sulphonic acid.
Chromotrope 2B	-	-	<i>p</i> -Nitraniline + 1 : 8 : 3 : 6-dioxynaphthalene disulphonic acid.
Diamond yellow R	-	-	Anthranilic acid + salicylic acid.
Milling yellow	-	-	2-Naphthylamine sulphonic acid + salicylic acid.

It has recently been found possible to prepare complex chromium and copper derivatives of dyestuffs of this type (neolan and palatine fast dyes).

## Dyes used in the Manufacture of Lakes

One of the best known is Lithol red (2-naphthylamine-1-sulphonic acid +  $\beta$ -naphthol) (B.A.S.F., English Patent, 25,511, 1899).

Other typical combinations are:—

*o*-Nitraniline-*p*-sulphonic acid or *p*-nitraniline-*o*-sulphonic acid +  $\beta$ -naphthol (M.L.B., English Patent, 16,409, 1901).

Aniline, etc. + 2 : 3-oxynaphthoic acid (Akt. Ges. für Anilin Fabrikation, English Patent, 1,235, 1903).

2-Naphthylamine disulphonic acids + naphthol sulphonic acids (Bayer, English Patent, 12,512, 1904).

Nitrochloranilines +  $\beta$ -naphthol (B.A.S.F., English Patents, 6,227, 1907, and 6,228, 1907).

## Direct Cotton Dyes

Most of the azo dyes mentioned above are not suitable for dyeing cotton directly. Until 1884 there was no synthetic dye which would fulfil this requirement, although natural dyestuffs such as safflower, tumeric and Orleans were known. In this year Böttiger discovered Congo red, which would dye cotton directly. This discovery was followed by many others. The dyeing of cotton by substantive dyes appears to depend on absorption and then precipitation of the colloidal dye-stuff. Salt added during the operation facilitates this process.

The combination of diazotised dehydrothiotoluidine sulphonic acid or primuline (see p. 478) with various components give cotton dyes, *e.g.*—

Oriol yellow—primuline + salicylic acid.

Rosophenine 10B—dehydrothiotoluidine sulphonic acid + 1-naphthol-4-sulphonic acid.

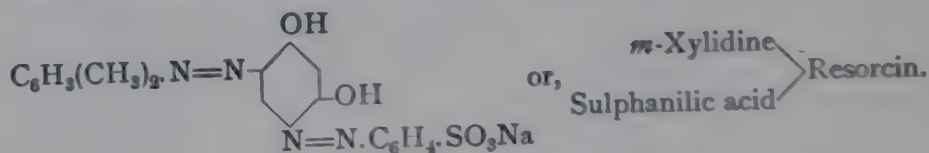
Various derivatives of 2 : 5 : 7-aminonaphthol sulphonic acid when combined with diazo compounds (aniline, toluidine, xylydine, naphthylamines, etc.) give cotton dyes, *e.g.*—

2-acetylamino-5-naphthol-7-sulphonic acid, 2-benzoylamino-5-naphthol-7-sulphonic acid, aminobenzoyl-2-amino-5-naphthol-7-sulphonic acids, aminophenyl-1 : 2-naphthothiazole-5-oxy-7-sulphonic acids, aminophenyl-1-2-naphthiminazole-5-oxy-7-sulphonic acids, etc.

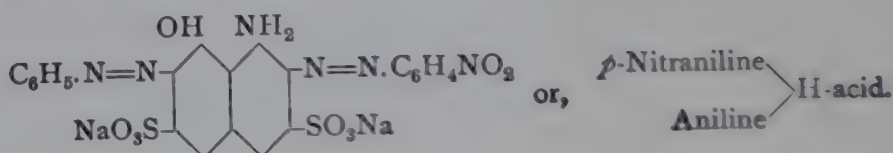
Disazo Dyes,  $R.N = N.R'.N = N.R''$ 

There are three main types of disazo dyes: (a) primary, (b) secondary, (c) disazo dyes from tetrazotised diamines.

(a) **Primary Disazo Dyes**.—Certain azo dye components can be coupled with two diazo groups; such components are phenol, resorcin,  $\alpha$ -naphthol,  $m$ -phenylenediamine,  $m$ -toluylendiamine,  $m$ -aminophenol, the aminonaphthol sulphonic acids referred to above, which can be coupled in acid or alkaline solution yielding different products, and the 1:8-dioxynaphthalene-4-sulphonic acid or -3:6-disulphonic acid. To prepare the primary disazo dyes, two molecular proportions of an amine, or one molecular proportion of each of two different amines, are diazotised and coupled with one molecular proportion of the second component. Thus **Resorcin Brown** is obtained by coupling  $m$ -xylidine (1 molecule) and sulphanilic acid (1 molecule) with resorcin (1 molecule).



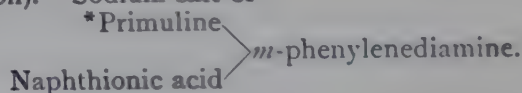
**Naphthol Blue-Black** is obtained by coupling 1:8-aminonaphthol 3:6-disulphonic acid (H acid) first with  $p$ -nitraniline in acid solution, and then with aniline in alkaline solution.



It dyes wool in an alkaline bath.

Other primary disazo dyes are—

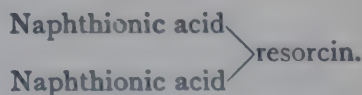
**Terracotta F** (dyes cotton).—Sodium salt of—



**Cotton Orange R** (dyes cotton)—



**Fast Brown** (acid wool dye)—



(b) **Secondary Disazo Dyes** are obtained by coupling diazotised aminoazo compounds with amines, phenols, etc. In order, therefore, to prepare bodies of this type it is necessary to diazotise *twice*—first an amine is diazotised, then the diazo salt thus produced is coupled directly to another amine—the “middle” component—and the amino group in the aminoazo body thus produced is then diazotised, and finally the product thus obtained is coupled with an amine, phenol, etc.

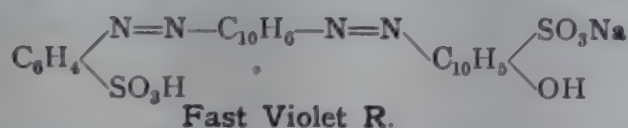
The amines employed as “middle components” must be of such a nature that when combined with the first component they can be rediazotised to yield a diazo salt. Thus the amines generally employed are those which, on coupling with the first component, give either para-aminoazo compounds, or aminoazo compounds containing the amino and azo groups in different nuclei; examples of the first type are aniline,  $o$ - and  $m$ -toluidine,  $p$ -xylidine,  $o$ -anisidine, cresidine,  $\alpha$ -naphthylamine and its 6- and 7-sulphonic acids (**Clève's acids**); examples of the second type are 2:5:7- and 2:8:6-aminonaphthol sulphonic acids, combined in alkaline solution, and the recently discovered derivatives of aminonaphthol sulphonic acids containing a heteronuclear amino group, such as the aminophenyl-1:2-naphthiminazoleoxy-sulphonic acids, and the aminobenzoylaminonaphthol sulphonic acids.



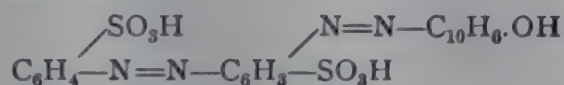
An example of such dyes is **Fast Violet R**, produced by (1) diazotising sulphanilic acid; (2) coupling the diazo compound with  $\alpha$ -naphthylamine, giving

$$\text{C}_6\text{H}_4 \begin{cases} \text{N}=\text{N}-\text{C}_{10}\text{H}_6\cdot\text{NH}_2 \\ \text{SO}_3\text{H} \end{cases};$$

(3) diazotising once again; and (4) coupling with  $\beta$ -naphthol sulphonic acid S, thus obtaining the dye—



**Biebrich Scarlet** is prepared by coupling aminoazobenzene disulphonic acid with  $\beta$ -naphthol, and has, therefore, the constitution—



Other secondary disazo dyes are—

**Brilliant Croceine M** (acid wool dye).—Aminoazobenzene + 2 : 6 : 8-naphtholdisulphonic acid.

**Cloth Scarlet G** (acid wool dye).—Aminoazobenzenesulphonic acid +  $\beta$ -naphthol.

**Croceine Scarlet 7B** } (acid wool dye).—Aminoazotoluene sulphonic acid + 2 : 8-naphtholsulphonic acid.  
 „ „ 8B }

**Diaminogen** (dyes unmordanted cotton blue).—Acetyl-1 : 4-naphthylenediamine-6- and -7-sulphonic acid +  $\alpha$ -naphthylamine + 2 : 6-naphthol sulphonic acid (product saponified).

**Janus Red** (dyes cotton and wool).—*m*-Aminophenyltrimethylammonium chloride + *m*-toluidine +  $\beta$ -naphthol.

**Naphthylamine Black D** (acid wool dye).—Naphthylamine disulphonic acid +  $\alpha$ -naphthylamine +  $\alpha$ -naphthylamine.

**Ponceau 4RB** } (dyes wool and cotton).—Aminoazobenzene sulphonic acid + 2 : 8-naphthol  
**Croceine Scarlet 3B** } sulphonic acid.

Recently a number of secondary disazo dyes have been prepared having 2 : 5 : 7-aminonaphthol sulphonic acid and its alkyl, aryl, acidyl, etc., derivatives as end components. These dye cotton blue to violet shades. (See English Patents, Nos. 14,248, 1907; 4,767, 1909; 4,768, 1909; 11,364, 1909.)

(c) **Disazo Dyes from Tetrazotised Diamines.**—This type of disazo dyes is prepared by tetrazotising, *i.e.*, diazotising both the amino groups of a primary diamine and combining the tetrazo compound so obtained either with two molecular proportions of one dye component or with one molecular proportion of one component and one molecular proportion of another component; in the first case the dyes are referred to as “symmetrical” and in the second case as “mixed” disazo dyes.

The most important diamines in this connection are the so-called para-diamines, of which benzidine,  $\text{H}_2\text{N}-\text{C}_6\text{H}_4-\text{C}_6\text{H}_4-\text{NH}_2$ , is typical; other well-known diamines of the benzidine type are *o*-tolidine, dianisidine, diethoxybenzidine, benzidine-*o*-disulphonic acid, benzidine sulphone. Similar diamines containing two benzene nuclei connected by another group and containing in each nucleus an amino group, usually in the para-position to the connecting group, are diaminostilbene disulphonic acid, *p*-diaminodiphenylurea, azoxyaniline, etc. The dyes derived from these diamines possess in general the highly important property of dyeing cotton directly (*i.e.*, without mordants), and hence are known as **direct or substantive cotton dyes**.

It should be noted, however, that the dyes derived from *m*-tolidine, *m*-dichlorbenzidine and benzidine-*m*-disulphonic acid do not dye cotton, but are acid wool dyes. It should be noted further that all diamines cannot be tetrazotised—thus ortho- and peri-diamines do not yield tetrazo salts but ring compounds, azimides. Some meta-diamines, *e.g.*, *m*-phenylenediamine, can be tetrazotised

like the paradiamines. The case of *p*-phenylenediamine requires special mention; this body cannot be readily tetrazotised; accordingly disazo dyes are prepared from this body by first diazotising *p*-nitraniline or an acidyl- (*e.g.*, acetyl) -*p*-phenylenediamine, combining the diazo compound with a dye component, reducing the nitro group or saponifying the acidylamino group, of the dye so obtained, then diazotising the amino group so produced and combining with a second molecule of a dye component. A similar process is employed with the sulphonic acids of 1 : 4-naphthylenediamine.

The following are typical dyes of this class; except where otherwise stated, they dye unmordanted cotton:—

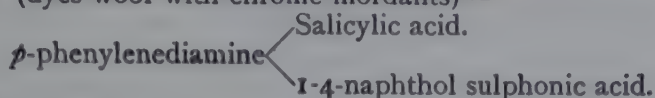
a. DERIVED FROM BENZIDINE AND ITS DERIVATIVES

Benzopurpurine B	. . .	Tolidine	2-naphthylamine-6-sulphonic acid.
			2-naphthylamine-6-sulphonic acid.
" 4B	. . .	Tolidine	naphthionic acid.
			naphthionic acid.
" 6B	. . .	Tolidine	1-naphthylamine-5-sulphonic acid.
			1-naphthylamine-5-sulphonic acid.
" 10B	. . .	Dianisidine	naphthionic acid.
			naphthionic acid.
Congo Blue 2B	. . .	Dianisidine	1-naphthol-4-sulphonic acid.
			2-naphthol-3 : 6-disulphonic acid.
Congo Corinth G	. . .	Benzidine	naphthionic acid.
			1-naphthol-4-sulphonic acid.
" B	. . .	Tolidine	1-naphthol-4-sulphonic acid.
			1-naphthol-4-sulphonic acid.
Congo Red	. . .	Benzidine	naphthionic acid.
			naphthionic acid.
" 4R	. . .	Tolidine	naphthionic acid.
			resorcin.
Diamine Black BH	. . .	Benzidine	2 : 8 : 6-aminonaphthol sulphonic acid (alkaline coupling).
			1 : 8 : 3 : 6-aminonaphthol sulphonic acid (alkaline coupling).
Diamine Blue BB	. . .	Benzidine	1 : 8 : 3 : 6-aminonaphthol sulphonic acid (alkaline coupling).
			1 : 8 : 3 : 6-aminonaphthol sulphonic acid (alkaline coupling).
Diamine Brown B	. . .	Benzidine	salicylic acid.
			2-phenylamino-8-naphthol-6-sulphonic acid (alkaline coupling).
Diamine Red 3B } Deltapurpurine 7B }	. . .	Tolidine	2-naphthylamine-7-sulphonic acid.
			2-naphthylamine-7-sulphonic acid.
Dianol Brilliant Red } Toluylene Red . }	. . .	Dichlorbenzidine	2 : 3 : 6-naphthylamine disulphonic acid.
			2 : 3 : 6-naphthylamine disulphonic acid.
Oxamine Red	. . .	Benzidine	salicylic acid.
			2 : 5 : 7-aminonaphthol sulphonic acid (alkaline coupling).

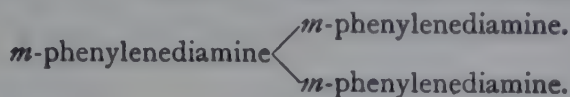


## b. DERIVED FROM PHENYLENE AND NAPHTHYLENE DIAMINES

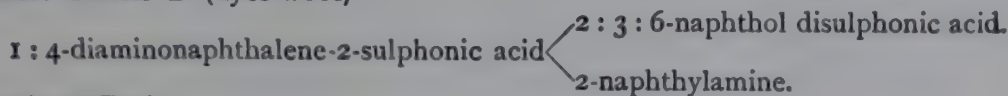
Azoalizarine Bordeaux W (dyes wool with chrome mordants)—



Bismarck Brown, Manchester Brown (dyes wool, leather, and tannin mordanted cotton)—



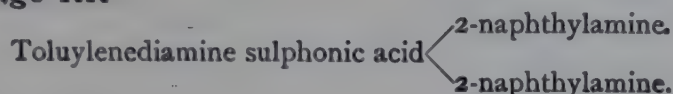
Coomassie Black B (dyes wool)—



Naphthylene Red—

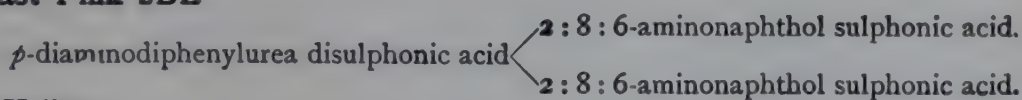


Toluylene Orange RR—



## c. DERIVED FROM OTHER DIAMINES

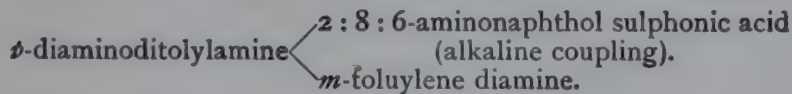
Benzo Fast Pink 2BL—



Brilliant Yellow—



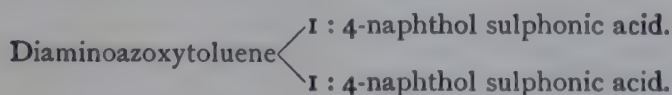
Diphenyl Fast Black—



Hessian Yellow—



St Denis Red—

Trisazo Dyes,  $R.N=N.R'.N=N.R''.N=N.R'''$ 

Dyes containing three azo groups can be produced in a variety of ways:—

## 1. From Secondary Disazo Dyes—

(a) Where the end component of a secondary disazo dye is an amine capable of diazotisation, it may be diazotised and coupled with another component.

EXAMPLE.—Acetyl-1:4-naphthylenediamine-7-sulphonic acid  $\rightarrow$  Clève's acid  $\rightarrow$  Clève's acid  $\rightarrow$  2:5:7-aminonaphthol sulphonie acid. (For Clève's acids, see p. 444.)

A similar dye is—



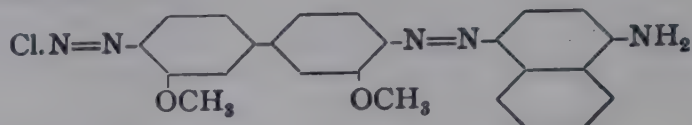
(b) When the end component of a secondary disazo dye is a component capable of combining with two azo groups, it may be combined with a further diazo compound. Similar products result on combining such a "double coupling" component with one molecular proportion of a diazoazo compound and one molecular proportion of a diazo compound.

EXAMPLE.—Chrome Patent Green A—  
 $p$ -aminosalicylic acid  $\rightarrow$   $\alpha$ -naphthylamine  $\rightarrow$  1 : 8 : 4 : 6-aminonaphthol sulphonic acid  $\leftarrow$  aniline.

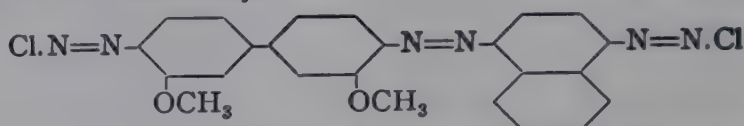
## 2. From Tetrazotised Diamines—

(a) By combining a tetrazotised diamine, such as benzidine, etc., with 1 molecule of a diazotisable middle component, *e.g.*,  $\alpha$ -naphthylamine, an intermediate compound is formed, which is then diazotised, thus giving a tetrazo body which is combined with two molecules of a component or one molecule of each of two components.

EXAMPLE.—Thus: dianisidine is tetrazotised and combined with 1 molecule of  $\alpha$ -naphthylamine, giving the intermediate compound—

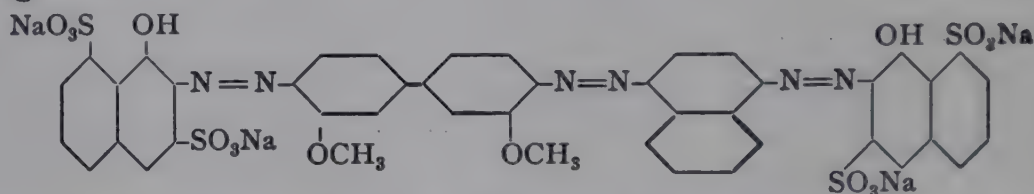


which is diazotised, and the tetrazo body—



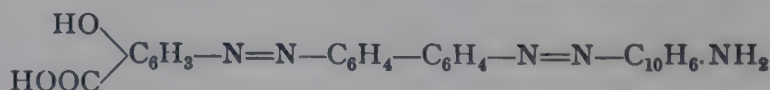
is combined with 2 molecules of 1-naphthol-3 : 8-disulphonic acid to form the trisazo dye—

### Congo Fast Blue B—

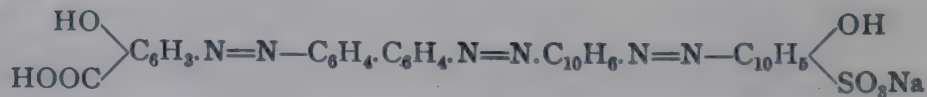


(b) If a tetrazotised diamine is combined with a molecule of a diazotisable amine and 1 molecule of another component to form a "mixed" disazo dye, the amino group of the middle component can then be diazotised and combined with an end component.

EXAMPLE.—Benzidine is combined with 1 molecule  $\alpha$ -naphthylamine and 1 molecule salicylic acid, giving—



The amino group is then diazotised and the diazo compound coupled with 1-naphthol-4-sulphonic acid, giving **Benzo Grey**—



The following are typical dyes produced by the methods 2a and 2b (above):—

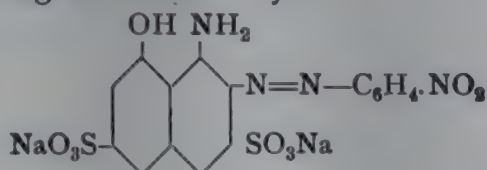
<b>Crumpsall Direct</b> <b>Fast Brown O</b>	}	Benzidine	salicylic acid.
			aniline $\rightarrow$ 2-phenylamino-8-naphthol-6-sulphonic acid.
<b>Diamine Beta Black</b>	}	Benzidine	1 : 8 : 3 : 6-aminonaphtholdisulphonic acid.
			$p$ -xylylene $\rightarrow$ 1 : 8 : 3 : 6-aminonaphtholdisulphonic acid.
<b>Diamine Bronze G.</b>	}	Benzidine	salicylic acid.
			1 : 8 : 3 : 6-aminonaphtholsulphonic acid $\rightarrow$ <i>m</i> -phenylenediamine.
<b>Oxamine Violet RR</b>	}	Benzidine	1 : 4-naphthol sulphonic acid.
			<i>m</i> -phenylenediamine oxamic acid $\rightarrow$ 1 : 4-naphthol sulphonic acid.

In each of the above processes, 2a and 2b, when  $p$ -phenylenediamine is employed, a procedure is adopted similar to that described under disazo dyes,  $p$ -nitraniline or acidyl- $p$ -phenylenediamine being the starting point, and the nitro

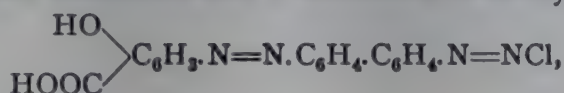


group being reduced, or the acidylamino group saponified at a suitable stage of the process. The process is similar in the case of 1:4-naphthylenediamine sulphonic acids.

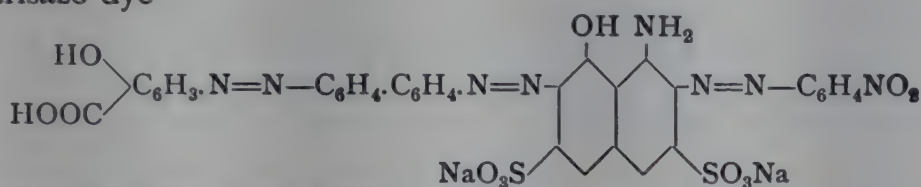
3. A further method may be illustrated by the dye **Diamine Green G**; *p*-nitraniline is diazotised and combined in acid solution with 1:8-aminonaphthol-3:6-disulphonic acid, giving the monazo dye—



This is then combined in alkaline solution with the intermediate compound from 1 molecule of tetrazotised benzidine and 1 molecule of salicylic acid—



giving the trisazo dye—



This dyes unmordanted cotton green shades.

Other dyes of this type are **Columbia Green**, **Diamine Green B**, **Diphenyl Green G** and **3G**, **Diamine Black HW**, **Diamine Black R**. All these are direct cotton dyes.

A similar method consists in taking a primary disazo dye in which, say, *p*-nitraniline or acet-*p*-phenylenediamine is one of the diazo components, reducing or saponifying, diazotising the free amino group so produced and combining with a component. Thus, a 1:8-aminonaphthol, -dioxynaphthylene, or -naphthylenediamine sulphonic acid is combined with 1 molecule diazo compound and 1 molecule *p*-nitraniline or acetyl-*p*-phenylenediamine, the product reduced or saponified, diazotised, and combined with amines or phenols.

Another type is afforded by 1:8:4-aminonaphthol sulphonic acid which can combine with 3 molecules of a diazo compound.

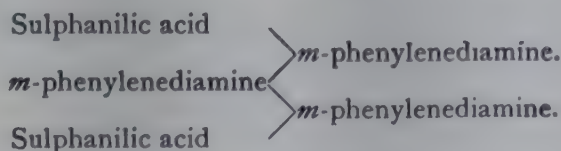
Finally, we may note a case in which a triamine is diazotised and combined with 3 molecules of a component—



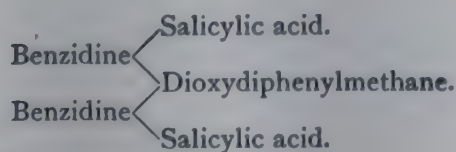
### Tetrakisazo Dyes, $R.N=N.R'.N=N.R''.N=N.R'''.N=N.R''''$

Here again various methods may be used A few examples are:—

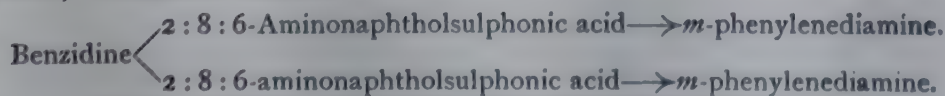
#### Benzo Brown G—



#### Mekong Yellow G—



#### Cuba Black, D<sup>1</sup>iamond Black—

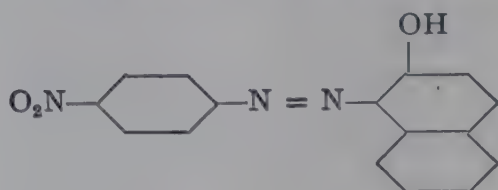


Higher polyazo dyes are known, but need not be discussed here, as they are not made or used to any great extent.

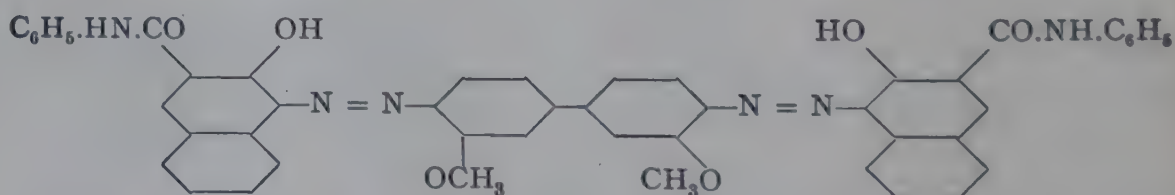
**Azo Dyes Produced on the Fabric—Ice-colours.**—Azo dyes have been produced directly on the fabric by impregnating the latter with the phenol (usually  $\beta$ -naphthol) in alkaline solution. The fabric is then wrung out and dried, later to be placed in a solution of a diazonium salt. Coupling takes place within the fibres of the yarn and in the majority of cases the resulting colour is well retained.

The name **ice-colour** has been given to the process because the majority of diazonium solutions require refrigeration to approximately  $0^\circ \text{C}$ . to inhibit premature decomposition.

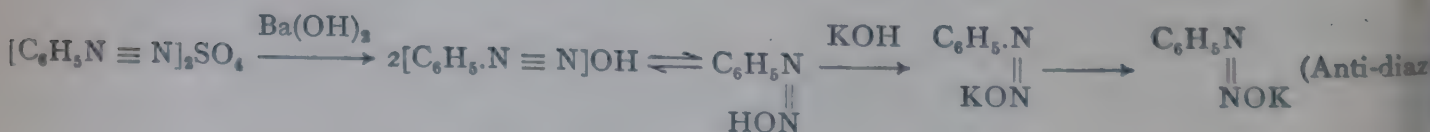
The first important compound of the **ice-colour** type was nitraniline red, prepared from *p*-nitraniline and  $\beta$ -naphthol in alkaline solution:



The many hundreds of similar dyes that followed cannot be mentioned here, but it is interesting to note one phenol, namely, naphthol AS (2-hydroxy-3-naphthoic acid anilide) which has the advantage that it may be coupled to diazonium salts on the wet cloth without previous drying to give a permanent insoluble colour, *e.g.*, tetra-azotised dianisidine coupled with naphthol AS, thus:—



In order to facilitate the use of diazonium salts by the dyer "anti-diazotates" are marketed (*cf.* syn-diazotates). Anti-diazotates are prepared from diazonium salts, *e.g.*, phenyl diazonium chloride, by treating with silver hydroxide giving a diazonium base or alternatively, phenyl diazonium sulphate and barium hydroxide giving barium sulphate instead of silver chloride and the diazonium base. These diazonium bases are very unstable and isomerise readily into the syn-diazotates which isomerise further to anti-diazotates on warming with alkali. The whole, rather complicated, process may be represented thus:—



These anti-diazotates are put on the market under such names as nitrosamine red (the anti-diazotate of *p*-nitraniline). The dyer then dissolves this in water and acidifies with mineral acid to obtain a coupling solution of the diazonium salt.

As diazonium salts are explosive, they are often mixed with aluminium sulphate or metallic salts of aromatic sulphonic acids to form a stable mixture for storage.

Other aids to rapid drying are the rapid fast dyes, rapidogen, or rapid azo dyes. These are mixtures of nitrosamine, or stabilised diazo salts with naphthol AS. These are largely used for printing.



### Developing Dyes

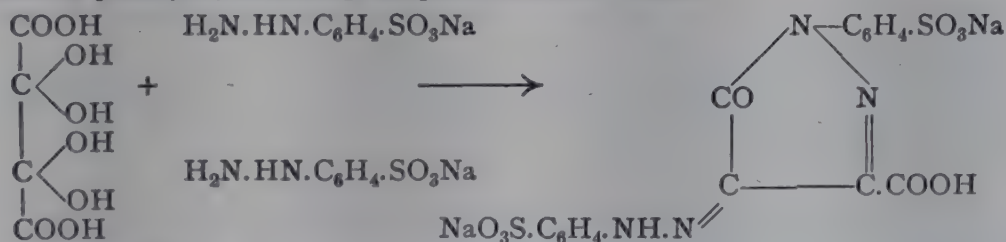
Many azo dyes are capable of conversion into azo dyes of a higher order by "development" on the fibre; the process is analogous to the production of **paranitraniline red** previously referred to (see pp. 442, 478, 545, 558).

Two cases arise: (a) when the end component of an azo dye is a diazotisable amine, the dye is applied to cotton and is then diazotised in a bath of nitrite and acid, and then passed through a bath containing  $\beta$ -naphthol or other component; (b) when the end component is a compound capable of combining with two azo groups, the dyed material is passed through a bath containing a diazo compound, e.g., diazotised *p*-nitraniline.

### Pyrazolone Dyes

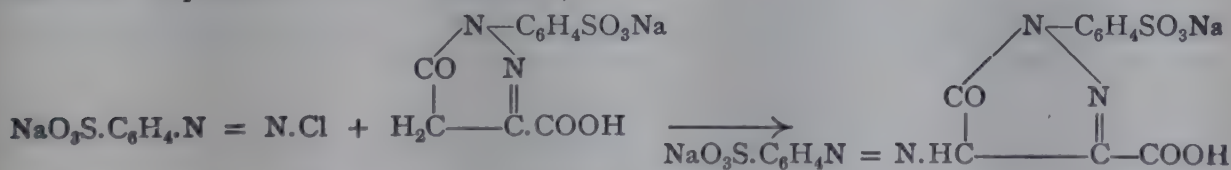
It will be convenient here to consider a group of dyes the constitution of which does not seem to be definitely established; from their method of preparation they may be regarded as containing either azo or hydrazone groups.

The prototype of these dyes is **Tartrazine**, a valuable yellow acid wool dye. Tartrazine was first prepared by condensing 1 molecule of dioxytartaric acid with 2 molecules of phenylhydrazine-*p*-sulphonic acid: thus—



i.e., the sodium salt of 1-*p*-sulphophenyl-3-carboxy-4-*p*-sulphophenylhydrazone-5-pyrazolone.

Tartrazine is also produced by condensing phenylhydrazine-*p*-sulphonic acid (1 molecule) with oxalacetic ester (1 molecule), which yields the ester of 1-*p*-sulphophenyl-3-carboxy-5-pyrazolone, saponifying this ester, and acting upon it with diazotised sulphanilic acid (1 molecule)—



This latter reaction suggests that tartrazine is an azo, not a hydrazone, compound.

A large number of similar dyes have been prepared recently by combining various diazo compounds with pyrazolones, such as the 1-*p*-sulphophenyl-3-carboxy-5-pyrazolone formulated above, the 1-*p*-sulphophenyl-3-methyl-5-pyrazolone, and the two corresponding pyrazolones containing no sulphonic group. Generally these dyes give bright yellow, orange, or red shades; many are suitable for dyeing wool, others serve as the starting point for lakes, while some which contain a residue of benzidine, etc., dye unmordanted cotton.


### Stilbene Dyes (see p. 544)

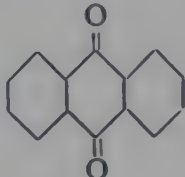
Dyes containing a stilbene residue and obtained by tetrazotising diaminostilbene disulphonic acid and coupling with components, have already been considered. There remains a group of dyes also containing the stilbene residue and probably containing azo groups, although they are not formed by the reactions of diazotising and coupling. On heating *p*-nitrotoluene sulphonic acid with aqueous caustic alkalis a complicated reaction (or series of reactions) occurs, the chief products of which are yellow dyes, known as **Curcumine S** or **Sun Yellow**, **Direct Yellow**, **Mikado Orange**, **Stilbene Yellow**, etc., which dye unmordanted cotton.

**Curcumine S** was formerly considered to be azoxystilbene disulphonic acid, and **Direct Yellow** dinitrosostilbene disulphonic acid, but according to Green and Crosland (*Journ. Chem. Soc.*, 89, 1602), these dyes are more complex and contain two stilbene groups, Stilbene Yellow 4G and 8G being dinitroazodistilbenedisulphonic acid, Direct Yellow being mainly azoazoxydistilbenedisulphonic acid, and Mikado Orange chiefly disazodistilbenedisulphonic acid.

A number of other dyes of this class have been prepared, but little is known of their constitution; **Polychromine B** and **Diphenyl Orange RR** are obtained by heating *p*-nitrotoluene sulphonic acid and *p*-phenylenediamine with caustic soda; **Curcuphenine** is similarly obtained from *p*-nitrotoluene sulphonic acid and dehydrothiitoluidine sulphonic acid.

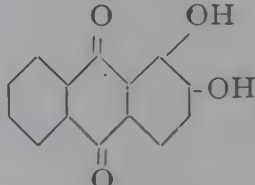
## 2. DYES DERIVED FROM ANTHRACENE

Under this heading are grouped a large number of dyes of varied structure and properties but possessing the common feature that the starting point in the preparation of each is anthracene,  $C_{14}H_{10}$ , , a residue or residues of this

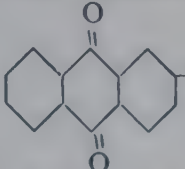
body or its oxidation product anthraquinone,  $C_{14}H_8O_2$ , , being always

present in the molecule of these dyes.

The first group of these dyes to be considered is the hydroxyanthraquinones of which alizarin is the prototype.

**Alizarin** or 1 : 2-dihydroxyanthraquinone, , is one of the oldest

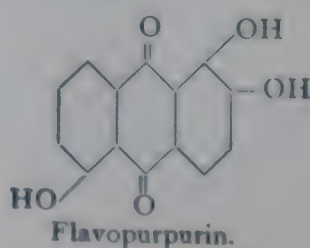
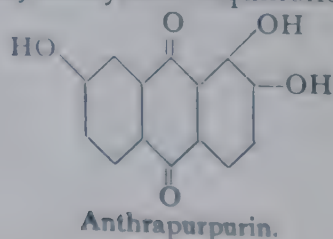
dyes in use and, after indigo, is perhaps the most important. It occurs in nature in madder in the form of a glucoside and was first obtained from this source. The natural alizarin is now almost entirely superseded by the synthetic product. Alizarin was first synthesised in 1868 by Graebe and Liebermann. In 1869 another and better synthesis was effected by them, and almost simultaneously by Perkin. This process consisted in sulphonating anthraquinone to produce the

$\beta$ -sulphonic acid,   $SO_3H$ . By fusing this body with caustic alkali the

sulphonic group is replaced by a hydroxyl group and at the same time another hydroxyl group enters in the  $\alpha$ -position. This process has since been improved by the addition of oxidising agents, such as  $KClO_3$ , to the alkali, and this is now the usual process for preparing this dye. Alizarin is a mordant dye giving different shades with various mordants. Its chief application is for dyeing bright yellowish red shades on cotton mordanted by Turkey red oil (see p. 43) and alumina by steeping in a bath of aluminium acetate or sulphate.

Closely related to alizarin are two trihydroxyanthraquinones:—

**Anthrapurpurin**, 1 : 2 : 7-trihydroxyanthraquinone, and **Flavopurpurin**, 1 : 2 : 6-trihydroxyanthraquinone:—



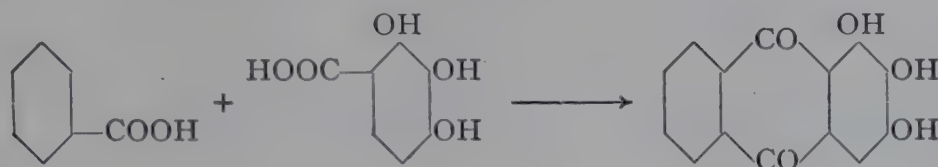


These bodies are obtained by fusing with caustic alkalis the disulphonic acids which are obtained by sulphonation of anthraquinone.

Commercial alizarin often contains one or both of these bodies, since the anthraquinone sulphonic acid used for the manufacture of alizarin often contains a certain amount of the disulphonic acids. Both these trihydroxyanthraquinones dye alumina-mordanted cotton red shades.

A third trihydroxyanthraquinone, **Purpurin**, 1 : 2 : 4-trihydroxyanthraquinone, which occurs with alizarin in madder, is obtained by oxidising alizarine by manganese dioxide and sulphuric acid, and also dyes red shades with alumina mordants.

A fourth trihydroxyanthraquinone, **Anthragallol**, 1 : 2 : 3-trihydroxyanthraquinone, is obtained by an entirely different process, viz., condensation of gallic acid with benzoic or phthalic acid, *e.g.* :—



It dyes brown with chrome mordants.

**Mordant Dyes and Chromo-dyes.**—In order that a dye shall be fixed by a metallic mordant it must possess the power of combining with the mordant to form a metal-dye complex—a chemical bond. These complexes are called lakes.

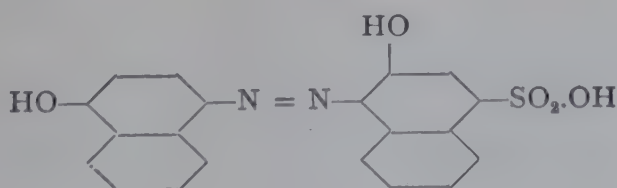
Most mordant dyes contain a hydroxyl or methoxyl group adjacent to the diazo group and form the metal complex in the following way :—



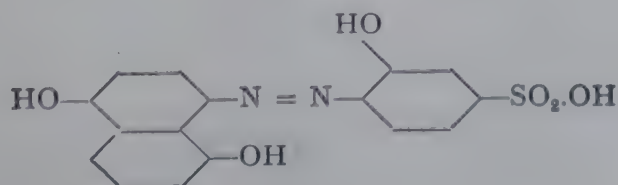
Azo dyes derived from the *o*-amino phenols possess the property of becoming several shades darker on treatment with potassium dichromate. This is thought to be partial oxidation of the dyes as well as the formation of a chromium metal complex as described above. This process is called chroming.

Some examples of chrome-mordanted dyes are

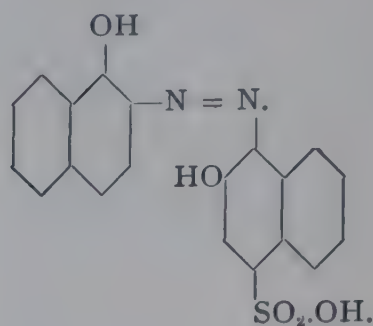
**Eriochrome blue-black,**



**Diamond black PV.** (Turns blue-black on chroming.)



## Eriochrome blue-black B,



The pure chromium and copper salts of dyes of this type are articles of commerce and are sold under the names, neolan dyes and palatine fast dyes.

**Alizarin Bordeaux**, 1 : 2 : 5 : 8-tetrahydroxyanthraquinone, is obtained by treating alizarin with fuming sulphuric acid, whereby a sulphuric ester of the tetrahydroxy body is first formed, and is then saponified; it dyes wool bordeaux with alumina mordants, and violet-blue with chrome mordants.

**Alizarin Cyanine R**, 1 : 2 : 4 : 5 : 8-pentahydroxyanthraquinone, is formed by oxidising **Alizarin Bordeaux** by various oxidising agents, *e.g.*, manganese dioxide in sulphuric acid, arsenic acid, lead peroxide, persulphates, nitric acid, or by electrolytic oxidation; it dyes blue to violet shades with mordants.

Similar oxidation of this pentahydroxy body gives a hexahydroxyanthraquinone:—

**Anthracene Blue**, 1 : 2 : 4 : 5 : 6 : 8-hexahydroxyanthraquinone, is obtained by treating with sulphuric acid and sulphur sesquioxide, 1 : 5 or 1 : 8-dinitroanthraquinone, or the mixture of these two bodies formed by nitrating anthraquinone; apparently the nitro groups are reduced to amino groups, which are then replaced by hydroxyl groups, while the other hydroxyl groups enter the molecule; the dyeing properties of this dye are similar to those of Alizarin Cyanine R.

**Rufigallol**, 1 : 2 : 3 : 5 : 6 : 7-hexhydroxyanthraquinone, is obtained by condensation of 2 molecules of gallic acid (*cf.* **Anthragallol** above); it dyes brown with chrome mordants.

It will be noticed that all the above-described hydroxyanthraquinones are mordant dyes, and all contain at least two hydroxy groups in ortho-position to one another; probably the property of forming lakes with mordants is dependent upon this structure. The dihydroxyanthraquinones isomeric with alizarin, *e.g.*, **quinizarin** (1 : 4), **anthrarufine** (1 : 5), **chrysazine** (1 : 8), **anthraflavic acid** (2 : 6), do not possess dyeing properties.

We have now to consider a number of dyes which are derivatives of the hydroxyanthraquinones.

**Alizarin Brown**,  $\alpha$ -nitroalizarin ( $\text{OH} : \text{OH} : \text{NO}_2 = 1 : 2 : 4$ ), is produced by nitrating alizarin in fuming sulphuric acid or in sulphuric acid containing arsenic acid, or by nitrating mono- or di-benzoylalizarin in sulphuric acid; nitration of alizarin in sulphuric acid containing boric acid gives **Alizarin Orange**,  $\beta$ -nitroalizarin ( $\text{OH} : \text{OH} : \text{NO}_2 = 1 : 2 : 3$ ); nitration of flavopurpurin gives **Alizarin Orange G** ( $\text{OH} : \text{OH} : \text{OH} : \text{NO}_2 = 1 : 2 : 6 : 3$ ). Reduction of  $\alpha$ -nitroalizarin gives  $\alpha$ -aminoalizarin, **Alizarin Garnet R**; **Alizarin Maroon** is a mixture of aminoalizarin and aminopurpurins, and is produced by nitrating commercial alizarin and then reducing.

Sulphonation of alizarin gives alizarin monosulphonic acid, **Alizarin Red S** ( $\text{OH} : \text{OH} : \text{SO}_3\text{H} = 1 : 2 : 3$ ). Sulphonation of flavopurpurin gives **Alizarin Red 3WS** ( $\text{OH} : \text{OH} : \text{OH} : \text{SO}_3\text{H} = 1 : 2 : 6 : 3$ ).

The above simple nitro-, amino-, and sulphonic derivatives are also mordant dyes.

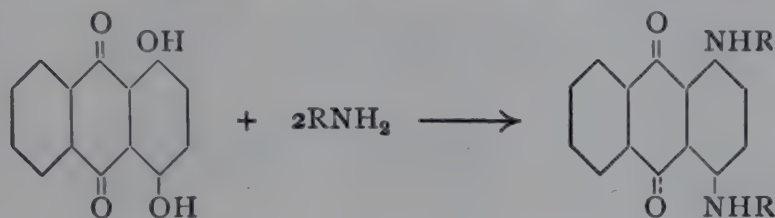
The bodies next to be discussed are acid wool dyes dyeing without mordants, though some can be subsequently chromed.



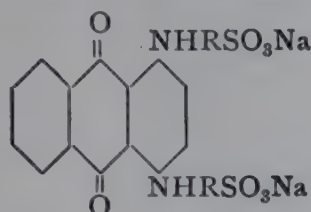
**Alizarin Saphirol B**, diaminoanthrarufin disulphonic acid, is produced by sulphonating anthrarufin, nitrating, and finally reducing.

Sulphonation and nitration of anthrachrysone (1 : 3 : 5 : 7-tetrahydroxy-anthraquinone) gives **dinitroanthrachrysone disulphonic acid** dyeing brown shades; reduction gives the corresponding diamino bodies which dye violet; boiling the last named with alkali gives a hexahydroxyanthraquinone disulphonic acid, **Acid Alizarin Blue BB and GR**.

An important property of the anthraquinone derivatives is the readiness with which negative substituents (Br, Cl, NO<sub>2</sub>, OH, SO<sub>3</sub>H) and also amino groups can be replaced by substituted amino groups NHR, where R is an alkyl or aryl radical. This reaction is applied in the production of a number of wool dyes; for example, quinizarin when condensed with aniline, *p*-toluidine, etc., gives—



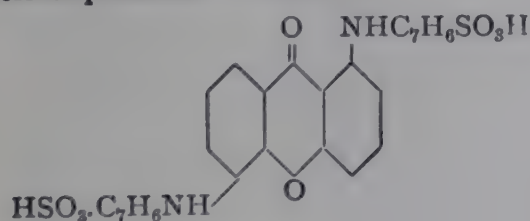
Sulphonation of these compounds gives **Quinizarin Greens**—



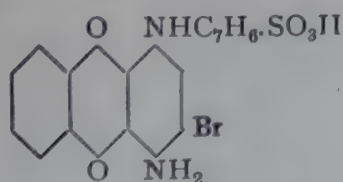
**Leuco Quinizarin**,  $\left( \begin{array}{c} \text{OH} \quad \text{OH} \\ | \quad | \\ \text{C}_6\text{H}_2\text{C}_6\text{H}_2\text{C}_6\text{H}_2 \\ | \quad | \\ \text{OH} \quad \text{OH} \end{array} \right)$ , gives the same products, the two meso-hydroxy groups being reoxidised to keto groups.

Other dyes of this type are—

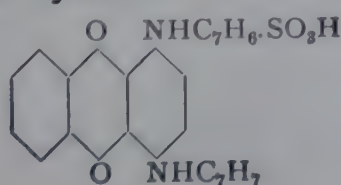
**Anthraquinone Violet**—



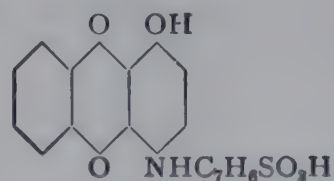
**Alizarin Pure Blue**—



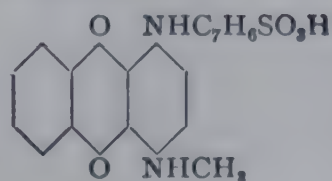
**Alizarin Cyanine Green**—



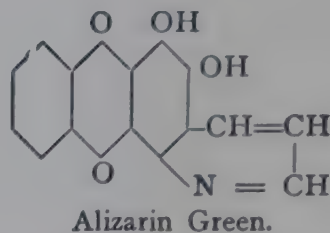
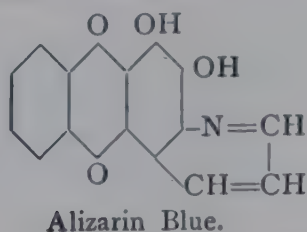
**Alizarin Irisol**—



**Alizarin Astrol**—



Another type of anthraquinone derivative is that in which a nitrogen-containing ring is added to the anthracene nucleus—the **anthraquinolines**; these are obtained from nitro- or amino-hydroxyanthraquinones by Skraup's quinoline synthesis, viz., by treating these bodies with glycerol and sulphuric acid; in this manner  $\beta$ -nitro- or  $\beta$ -aminoalizarin gives **Alizarin Blue**, while  $\alpha$ -aminoalizarin gives **Alizarin Green**—



Both these compounds give soluble bisulphite compounds, **Alizarin Blue S** and **Alizarin Green S**, on treatment with sodium bisulphite, which are used in printing with chrome mordants.

A similar quinoline compound, **Alizarin Black P**, and its bisulphite combination, **Alizarin Black S**, are obtained from  $\beta$ -nitro- or  $\beta$ -amino-flavopurpurin.

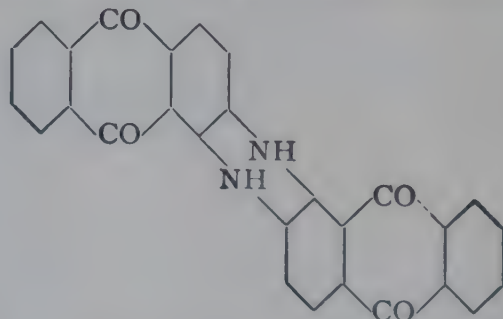
Treatment of Alizarin Green with strong sulphuric acid at high temperatures produces a 1 : 2 : 5 : 7 : 8-pentahydroxyanthraquinoline, **Alizarin Indigo Blue**, which also gives a soluble bisulphite compound, **Alizarin Indigo Blue S**; concentrated or fuming sulphuric acid with Alizarin Blue gives 1 : 2 : 5 : 8-tetrahydroxyanthraquinoline, **Alizarin Green**, bisulphite compound **Alizarin Green S**.

### Recent Developments in Anthracene Dyes—Anthracene Vat Dyes

In recent years there has been a great development in the anthracene dyes, chiefly in the production of the so-called "vat" dyes, *i.e.*, dyes which, like indigo, are insoluble, or practically so, in water, but yield on reduction colourless or slightly coloured "leuco" compounds which are soluble in alkali. The fabric to be dyed is impregnated with a solution of the leuco compound, and the dye is developed by oxidation in air or otherwise.

**Vat Dyes derived from Anthracene.**—The oldest anthracene vat dye is **Indanthrene**, **Indanthrene Blue R**, which is prepared by melting 2-aminoanthraquinone with caustic alkali (B.A.S.F., English Patents, 3,239, 1901; 22,762, 1901).

Indanthrene is N-dihydro-1 : 2 : 1' : 2'-anthraquinoneazine—



and dyes blue shades.

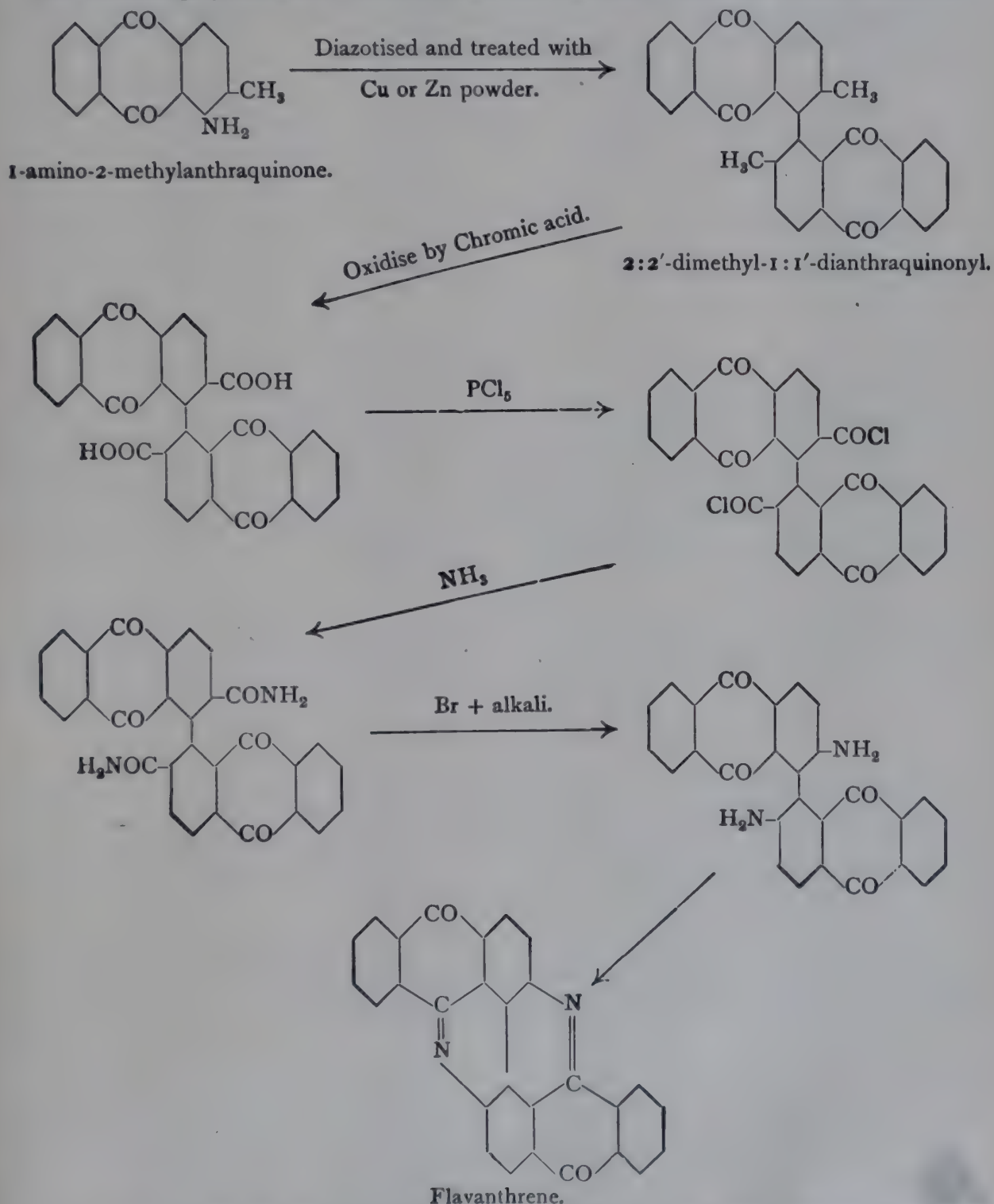
Indanthrene can also be prepared by condensing 1-amino-2-halogenanthraquinone (or 2-amino-1-halogenanthraquinone) with itself (F. v. Bayer, English Patent, 7,692, 1904); by condensing 1 : 2-diaminoanthraquinone with 1 : 2-anthraquinone and oxidising the product (F. v. Bayer, English Patent, 12,756, 1905); by condensing 1 : 2-diaminoanthraquinone with alizarin (F. v. Bayer, English Patent, 9,102, 1906); and together with Flavanthrene (*v. infra*) by treating 1-aminoanthraquinone with acid condensing agents (B.A.S.F., English Patent, 19,322, 1906). Halogenised indanthrenes (**Indanthrene Blue GC, GCD, and CE**, etc.) are prepared by chlorinating or brominating indanthrene (B.A.S.F., English Patents, 4,035 1902; 23,179, 1903; 17,242, 1905). **Algol Blue K** (N-dimethylindanthrene) is made from 1-methylamino-2-bromanthraquinone by the second method mentioned above.



Indanthrene disulphonic acid (B.A.S.F., English Patent, 12,185, 1901) and monosulphonic acid (B.A.S.F., English Patent, 339, 1909) are also known, as well as other derivatives.

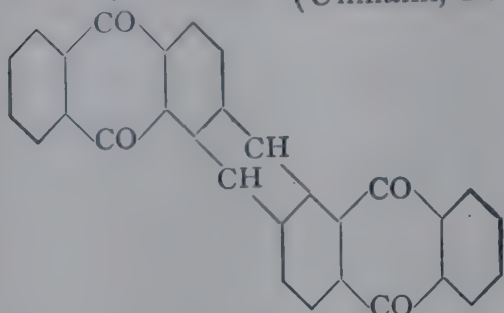
Another azine dye is **Flavanthrene** (Indanthrene Yellow) prepared by heating 2-aminoanthraquinone with alkali at a higher temperature than that required for Indanthrene; oxidising agents, *e.g.*, potassium nitrate, may be added to the melt; it is also obtained by heating 2-aminoanthraquinone with condensing agents, for instance, antimony pentachloride in nitrobenzene, or aluminium chloride alone, or by the action of acid oxidising agents, such as bichromate and sulphuric acid, manganese dioxide and sulphuric or nitric acid or lead peroxide (B.A.S.F., English Patent, 24,354, 1901). Flavanthrene dyes cotton blue shades which on standing become a bright yellow.

The following synthesis by Scholl (*Ber.*, 40, p. 1691) shows its constitution:—



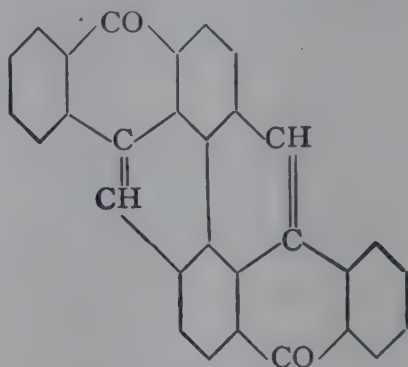
Analogous to Indanthrene and Flavanthrene, but containing methine groups in place of nitrogen, are **Anthraflavone** and **Pyranthrene**.

**Anthraflavone** —or the stilbenze derivative  $C_{14}H_7O_2 \cdot CH=CH \cdot C_{14}H_7O_2$   
(Ullmann, *Ber.*, 46, 712).



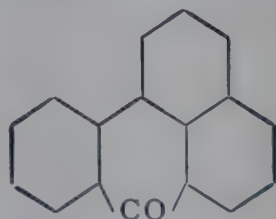
is prepared by treating 2-methylantraquinone or its  $\omega$ -halogen derivatives with condensing agents (B.A.S.F., English Patent, 10,677, 1905; D.R.P., 199,756); it dyes citron-yellow shades.

**Pyranthrone** (Indanthrene Gold Orange)—



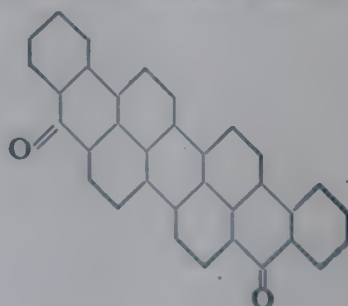
is prepared by treating 2:2'-dimethyl-1:1'-dianthraquinonyl with alkali or zinc chloride, with or without oxidation (B.A.S.F., English Patent, 14,578, 1905; Scholl, *Ber.*, 43, p. 346); it dyes orange tints. Treatment with halogens (English Patents, 10,505, 1906; 12,568, 1909) gives redder dyes.

The next group of dyes to be considered are the **benzanthrone** dyes. The benzanthrone are compounds containing the group—



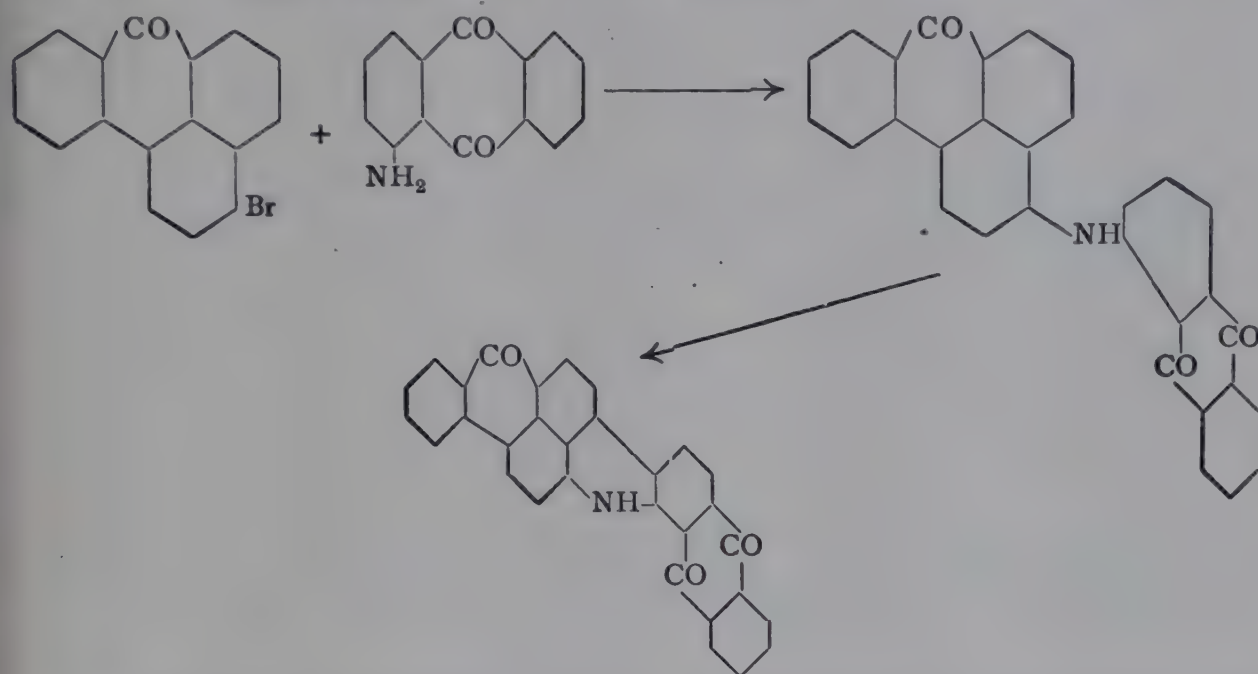
and are prepared by heating anthraquinone or its reduction products (anthranol, oxanthranol, or anthracene) or its amino, sulphonic, etc., derivatives with glycerin, preferably in presence of condensing agents, such as sulphuric acid. The benzanthrone undergo further condensation on being melted with alkalis, and yield blue to violet dyes (B.A.S.F., English Patent, 16,538, 1904; D.R.P., 176,018; Bally, *Ber.*, 38, p. 194).

The dye prepared from anthranol is known as **Violanthrene**, and that obtained from 2-aminoanthraquinone as **Cyananthrene**. Violanthrene has the formula of a dibenzanthrone (see English Patent, 16,271, 1910)—

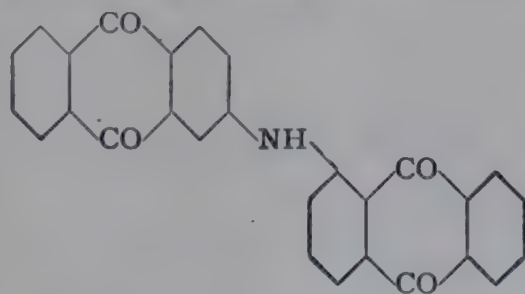




Among the derivatives of benzanthrone we may note: **benznaphthanthrone** from naphthanthraquinone (English Patent, 853, 1905) gives a reddish blue dye; **benzanthronequinolines** from  $\alpha$ -aminoanthraquinones (English Patent, 3,819, 1905) give violet-blue dyes; green dyes (**Indanthrene Green**, etc.) by nitrating benzanthrone dyes, with or without subsequent reduction (English Patent, 1,818, 1905); halogen derivatives from halogenanthraquinones (English Patent, 7,022, 1905), or by halogenising the dyes (English Patent, 22,519, 1905); the latter dye violet-blue to red-violet shades. Halogenised benzanthrone, on treatment with alkali, give dyes which usually contain no halogen, and are known as **isoviolanthrenes** (English Patent, 20,837, 1905). Other derivatives are obtained by heating aminobenzanthrones with metallic salts or oxides (English Patents, 10,770, 1907; 3,156, 1908). Brombenzanthrone condensed with 1-aminoanthraquinone gives benzanthrone-1-aminoanthraquinone, which, by treatment with condensing agents, gives a **green dye** (English Patent, 24,604, 1908; D.R.P., 212,471).



Another group of dyes is that containing two or three anthraquinone nuclei united by NH groups, the **dianthraquinonylamines** and **trianthraquinonylamines**,  $\alpha$ - $\beta$ -**Dianthraquinonylamine** (Algol Orange R)—



is prepared by condensing 2-aminoanthraquinone with 1-chloranthraquinone, or 1-aminoanthraquinone with 2-chloranthraquinone (D.R.P., 162,824; B.A.S.F., English Patent, 19,199, 1905); it dyes orange shades (F. v. Bayer, English Patent, 24,810, 1908).

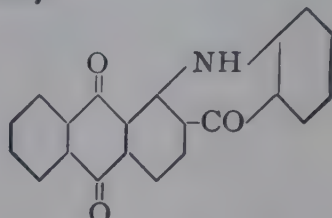
**Trianthraquinonylamines**, dyeing red shades, are produced by condensing two molecular proportions of 2-chloranthraquinone with 1:5-diaminoanthraquinone (**Indanthrene Bordeaux B**, B.A.S.F., English Patent, 10,324, 1906), or by condensing two molecular proportions of 1-aminoanthraquinone with  $\beta$ - $\beta$ -dihalogenanthraquinones (**Indanthrene Red G**, B.A.S.F., English Patent, 4,235, 1907). A number of derivatives of di- and tri-anthraquinonylamines giving a variety of shades are known (English Patents, 10,860, 1906; 13,057, 1906; 7,418, 1908; 12,167, 1908; 5,382, 1909; 9,219, 1909).

A further group of dyes is the **acidylaminoanthraquinones**, obtained by introducing the formyl, acetyl, benzoyl, succinyl, salicylyl, thiosalicylyl, anisyl, cinnamyl, etc., radicals into the amino groups of aminoanthraquinones (F. v. Bayer, English Patents, 2,709, 1909; 3,055, 1909); these dye yellow, red, orange, blue, violet, etc., shades (**Algol Yellows, Algol Reds**, etc.). **Helindon Yellow 3GN** (English Patent, 24,920, 1909), is a symmetrical urea derived from 2-aminoanthraquinone.

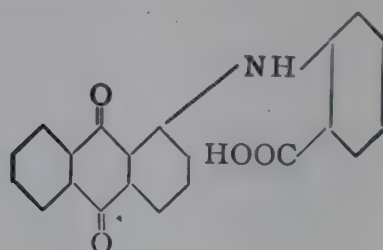
A number of anthracene vat dyes containing sulphur are also known, e.g. **mercaptans** (English Patent, 10,387, 1908), **thiazoles** (English Patent, 12,828, 1911), **thiazines** (English Patents, 18,240, 1911; 28,479, 1911), **thioureas** (English Patent, 11,473, 1910).

Two groups of dyes which are at present attracting attention are the **anthraquinone acridones** and **thioxanthones**.

**Anthraquinone 1 : 2-acridone,**

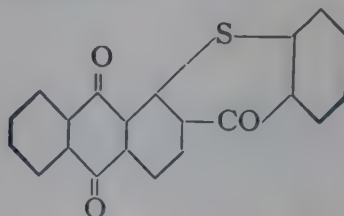


is prepared by condensing anthranilic acid with *α*-chlor- or *α*-nitro-anthraquinone and heating the resulting carboxyanilido-anthraquinone,



with condensing agents (Ullmann, English Patent, 12,653, 1909).

**Anthraquinone-1 : 2-thioxanthrone,**



is similarly prepared from thiosalicylic acid (Ullmann, English Patent, 30,480, 1909).

A number of derivatives of these dyes have been prepared (B.A.S.F., English Patent, 13,907, 1909, etc.).

### 3. DYES OF THE INDIGO, THIOINDIGO, AND INDIGOIII SERIES

#### Indigo (Indigo Blue, Indigotin)

Is the most important dye of commerce. It was originally obtained from natural sources, but the natural indigo has been very largely replaced by synthetic indigo the manufacture of which is perhaps the greatest triumph of dyestuff chemistry.

Indigo has the formula,  $C_{16}H_{10}N_2O_2$ , or It occurs

nature as a glucoside, **indican**, in various plants—*Indigofera tinctoria*, *Indigo an Polygonium tinctorium*, *Isatis tinctoria*. Hydrolysis of the indican gives indigo as a sugar, indiglucin; this hydrolysis is effected in practice by fermenting the leaves and stems of the indigo-bearing plants.



Indigo has been synthesised by a number of processes, only the more important of which can be dealt with here.

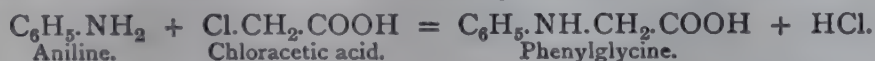
Baeyer in 1880 synthesised it from *o*-nitrocinnamic acid,  $\text{C}_6\text{H}_4 \begin{array}{l} \text{CH}=\text{CH}.\text{COOH} \\ \text{NO}_2 \end{array}$ . Treatment of this compound with bromine gives *o*-nitrodibromhydrocinnamic acid,  $\text{C}_6\text{H}_4 \begin{array}{l} \text{CHBr}-\text{CHBr}.\text{COOH} \\ \text{NO}_2 \end{array}$ , from which alkalis remove hydrobromic acid, giving *o*-nitrophenylpropionic acid,  $\text{C}_6\text{H}_4 \begin{array}{l} \text{C}\equiv\text{C}.\text{COOH} \\ \text{NO}_2 \end{array}$ ; this compound, on treatment with alkaline reducing agents, splits off carbon dioxide and condenses to indigo. An alternative method consists in treating *o*-nitrocinnamic acid with chlorine, which gives phenylchlorolactic acid,  $\text{C}_6\text{H}_4 \begin{array}{l} \text{CHOH}-\text{CHCl}.\text{COOH} \\ \text{NO}_2 \end{array}$ ; alkalis convert this compound into *o*-nitrophenyloxyacrylic acid,  $\text{C}_6\text{H}_4 \begin{array}{l} \text{O} \\ \diagup \quad \diagdown \\ \text{CH}-\text{CH}.\text{COOH} \\ \text{NO}_2 \end{array}$ , which condenses on heating in solution into indigo.

In 1882 Baeyer synthesised indigo from *o*-nitrobenzaldehyde; treatment of this body with acetone gives *o*-nitrophenyllactomethylketone,  $\text{C}_6\text{H}_4 \begin{array}{l} \text{CHOH}.\text{CH}_2\text{COCH}_3 \\ \text{NO}_2 \end{array}$ , which is converted into indigo by treatment with alkalis. These syntheses of Baeyer's were not, however, a commercial success, although *o*-nitrophenyllactomethylketone has been employed under the name of Indigo salt for producing indigo on the fibre (the bisulphite compound of the ketone being printed on the fibre which is then passed through an alkaline bath).

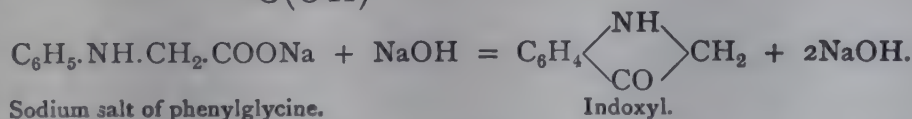
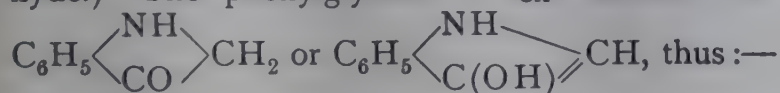
Heumann's synthesis of indigo in 1890 from phenylglycine, and soon afterwards from phenylglycine-*o*-carboxylic acid, led to the commercially successful placing of synthetic indigo upon the world's markets.

Two main processes are now worked on a very large scale:—

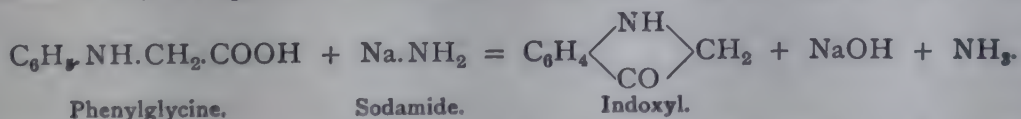
1. **The Phenylglycine Process**, worked by the Höchst Farbwerke, consists in heating aniline with chloracetic acid, when phenylglycine is formed, thus:—



(Phenylglycine has also been made by heating aniline with HCN and formaldehyde.) The phenylglycine is next melted with caustic soda to form indoxyl,



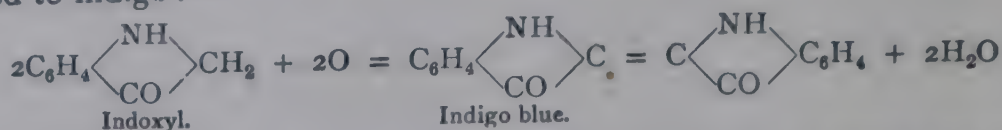
But since at the high temperature necessary for proper fusion a large portion of the parent materials are destroyed by the alkali, with a resulting poor yield of indoxyl, it is preferable to add materials to the caustic soda to lower the temperature of melting. A great improvement was effected by the Frankfurter Scheideanstalt by adding sodamide,  $\text{NaNH}_2$  (M.P.  $120^\circ \text{C}$ .; prepared by heating metallic sodium in a stream of dry  $\text{NH}_3$ , see p. 638), when the following change takes place:—



The escaping ammonia is collected and used again. Carbides and nitrides have also been used instead of sodamide. To obtain indigo the melt is dissolved in water, and air blown through to oxidise and condense the indoxyl (probably present in the alkaline solution as the sodium salt,  $\text{C}_6\text{H}_4 \begin{array}{l} \text{NH} \\ \diagup \quad \diagdown \\ \text{C}(\text{ONa}) \end{array} \text{CH}$ ) to indigo;

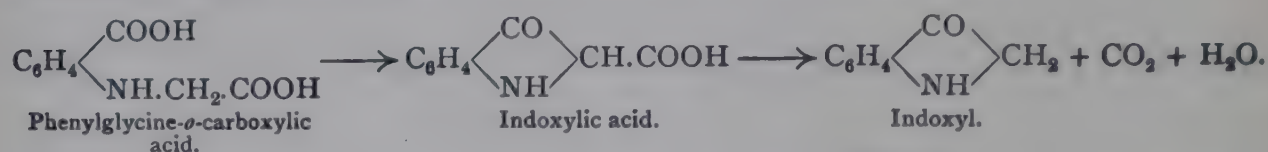


or the solution is acidified so as to give free indoxyl, which is then oxidised and condensed to indigo :—

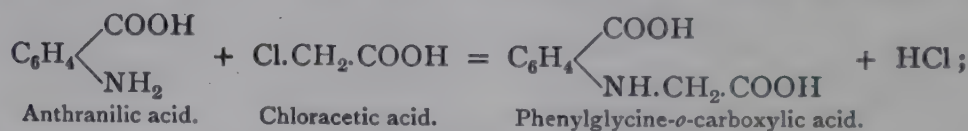


In this process the starting point is benzene (from which aniline is obtained by nitrating and reducing as described on p. 424), while intermediately chloracetic acid, caustic soda, and sodamide are used. The success of the synthesis depends entirely upon the price at which these materials are obtainable.

2. **The Phenylglycine-*o*-Carboxylic Acid Process**, worked by the Badische Anilin- und Soda-Fabrik, depends upon the fact that when phenylglycine-*o*-carboxylic acid is melted with caustic alkalies, it condenses, thus :—



The starting point in this process is **Anthranilic Acid**,  $\text{C}_6\text{H}_4\begin{array}{c} \text{NH}_2 \text{ (1)} \\ \diagup \quad \diagdown \\ \text{COOH} \text{ (2)} \end{array}$ , which the B.A.S.F. obtain from the cheap and abundant naphthalene by the following series of operations: (1) The naphthalene is oxidised to phthalic acid,  $\text{C}_6\text{H}_4(\text{COOH})_2$ , by heating with concentrated sulphuric acid and mercury (see **Phthalic Acid**, p. 430), when the anhydride of the acid distils over; (2) the phthalic anhydride,  $\text{C}_6\text{H}_4\begin{array}{c} \text{CO} \\ \diagup \quad \diagdown \\ \text{CO} \end{array}\text{O}$ , thus obtained is converted into phthalimide,  $\text{C}_6\text{H}_4\begin{array}{c} \text{CO} \\ \diagup \quad \diagdown \\ \text{CO} \end{array}\text{NH}$ , by heating with ammonia; which (3) on treating with bleaching powder or NaOCl gives anthranilic acid,  $\text{C}_6\text{H}_4(\text{COOH})(\text{NH}_2)$  (see p. 430); (the anthranilic acid may also be obtained by heating *o*-chlorbenzoic acid,  $\text{C}_6\text{H}_4\text{Cl}.\text{COOH}$  (1 : 2) with  $\text{NH}_3$  in the presence of Cu); (4) next, the anthranilic acid is treated with chloracetic acid to obtain phenylglycine-*o*-carboxylic acid—



and (5) the phenylglycine-*o*-carboxylic acid is finally converted into indoxyl and then into indigo as above described.

It has also been shown that for phenylglycine-*o*-carboxylic acid one may substitute methylanthranilic acid,  $\text{C}_6\text{H}_4\begin{array}{c} \text{COOH} \\ \diagup \quad \diagdown \\ \text{NH}.\text{CH}_3 \end{array}$ , when melting with sodamide for indoxyl. According to this latter process the use of chloracetic acid is abolished, since methylanthranilic acid may be produced directly from anthranilic acid by treating with methyl chloride, or from phthalic anhydride by treating with methylamine.

On comparing the two main processes for manufacturing synthetic indigo, it will be seen that the one starts from benzene, and the other from naphthalene. Both processes at present work with monochloracetic acid, thereby creating a huge demand for glacial acetic acid (about 3,000 tons are used annually, being obtained from the distillation of about 150,000 cub. yds. of wood). The chlorine for chlorinating the acetic acid is obtained by electrolysing alkali chlorides, which also produces caustic alkali. Finally the demand for a concentrated sulphuric acid for oxidising naphthalene to phthalic acid, coupled with the escape of large amounts of  $\text{SO}_2$  and  $\text{SO}_3$  during the heating process, contributed very essentially to the industrial development of the contact process for the manufacture of sulphuric acid. The manufacture of synthetic indigo thus furnishes a very interesting series of examples of the interaction of one branch of chemical industry on others.

The following statistics show that although **synthetic indigo** has largely diminished the culture of **natural indigo** in India and other tropical countries, yet the demand for indigo is also not increasing, probably owing to the competitive action of several very fast blue dyes, derived from anthracene, which are now on the market.



Imported into Great Britain :—

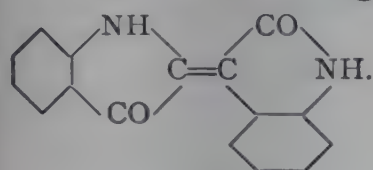
	1896.	1906.	1907.	1908.	1909.	1913.	Value. (1913).
		Cwt.	Cwt.	Cwt.	Cwt.	Cwt.	
Synthetic indigo - -	0	39,042	41,379	37,761	33,494	23,889	£76,695
Natural indigo - -	...	7,641	11,116	8,644	10,051	4,174	54,739

Practically all the synthetic indigo imported into Great Britain comes from Germany: (1910) **Germany**, 28,182 cwt. (value, £101,183); **Netherlands**, 4 cwt. (value, £16); **Belgium**, 10 cwt. (value, £50); **other countries**, *nil*. The total amount of synthetic indigo exported from Germany in 1909 amounted to 161,100 dz. = 16,110 metric tons, or roughly, 320,000 cwt. representing a value of 40.3 million marks (say £2,000,000).

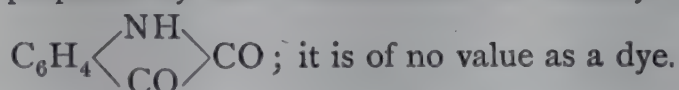
The United States imported of Indigo: 1906, 7,393,000 lbs.; 1910, 7,539,000 lbs.; value in 1910, \$1,196,000. Of this quantity Germany imports 7,000,000 lbs., value \$1,000,000.

Indigo is a typical vat dye, *i.e.*, before dyeing it is reduced to its leuco compound, indigo white,  $C_6H_4 \begin{matrix} \text{NH} \\ \diagup \quad \diagdown \\ \text{C}(\text{OH}) \end{matrix} = \text{C} - \text{C} = \begin{matrix} \text{NH} \\ \diagdown \quad \diagup \\ \text{C}(\text{OH}) \end{matrix} C_6H_4$ , which is soluble in alkalis; the fibre (cotton, wool, or silk) is immersed in an alkaline solution of this body, and is then withdrawn and oxidised to indigo by exposure to air. The old method of obtaining the vat was by fermentation by means of dung; other methods consisted in the use of glucose and alkali, lime and ferrous sulphate, or zinc and alkali; the vat is now usually prepared by means of sodium hydrosulphite and alkali.

**Indirubin or Indigo Red** is an isomer of indigo and has the constitution



It occurs as an impurity in natural indigo, and may be prepared by the condensation of indoxyl with isatin,



Sulphonation of indigo yields a disulphonic acid, **Indigo Carmine**, which is an acid wool dye.

### Halogenised Indigo Dyes

Halogenised indigo dyes, *i.e.*, indigo derivatives in which one or more of the hydrogen atoms of the benzene nuclei has or have been replaced by bromine or chlorine, may be prepared by two general methods:—

1. Treatment of indigo or a derivative thereof, either alone or suspended or dissolved in various media, with halogen or with halogenising agents.
2. Obtaining a halogenised parent material, *e.g.*, brom- or chlor-phenylglycine-*o*-carboxylic acid, which is then subjected to suitable treatment, say condensation and oxidation, to yield a halogenised dye.

These two methods have been known for some years, but until 1907 had only been applied to the production of mono- and di-halogen derivatives, except as regards a tetrachlorindigo prepared in 1901 from dichlorinated phenylglycine-*o*-carboxylic acid (B.A.S.F., English Patent, 20,552, 1901).

From 1907 onwards both methods have been largely extended, and halogen-indigos containing from 3 to 6 atoms of halogen in the molecule are now known.

By treating indigo, suspended in an inert medium such as nitrobenzene, with the theoretical amount of bromine (two atomic proportions of bromine for each bromine atom to be introduced into the indigo molecule), at a raised temperature, **tri-** and **tetra-bromindigos** are obtained (S.C.I.B., English Patent, 5,122, 1907; D.R.P., 193,438). By applying this method to mono- and di-chlorindigos, mixed tri- and tetra-halogenindigos are produced, and from the para-dihalogenindigos (*i.e.*, containing halogen in para position to the carbonyl group) penta- and hexa-halogenindigos result (S.C.I.B., English Patent, 10,326, 1907).

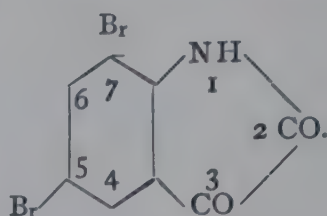


Chlorination of indigo in similar media in presence of chlorine carriers yields **tri- and tetra-chlorindigos** (S.C.I.B., English Patent, 19,793, 1908).

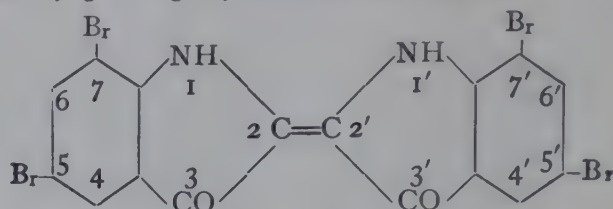
The above-described products dye reddish-blue shades.

The constitution of these bodies has been established by Grandmougin (*Ber.*, 42, p. 4408) in the following way:—

Tetrabromindigo obtained by bromination in nitrobenzene is oxidised by means of nitric acid to a dibromisatin of M.P.  $249^{\circ}$ - $250^{\circ}$  C., which is identical with the known 5 : 7-dibromisatin,



Distillation of the dibromisatin with potash gives 2 : 4-dibromaniline. The tetra-bromindigo is, therefore, 5 : 7 : 5' : 7'-tetrabromindigo,



The nomenclature here employed is that of Friedländer (*Ber.*, 42, p. 765). The di- and tri-bromindigos obtained similarly are the 5 : 5' and 5 : 7 : 5' bodies. The tetrabromindigo is known in commerce as **Ciba Blue**.\*

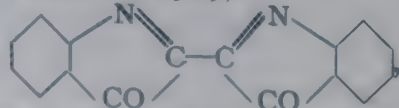
Another method of bromination consists in treating indigo suspended in concentrated sulphuric acid with bromine in the cold (F. v. Bayer, English Patent, 4,423, 1908). In this process the hydrobromic acid formed is partly oxidised by the sulphuric acid, so that less than the theoretical amount of bromine can be used; for the same reason bromides may be used instead of bromine in this process (F. v. Bayer, English Patent, 5,582, 1908). The tri- and tetra-bromindigos so obtained dye greenish-blue shades. Grandmougin asserts that they are identical with the products obtained by bromination in nitrobenzene (*Ber.*, 43, p. 937). A closely allied process is that of Kalle & Co. (English Patent, 15,088, 1909), in which chloresulphonic acid is used as the suspension medium during the bromination.

Another process (F. v. M.L.B., English Patent, 25,513, 1907) consists in treating dihalogenindigos with excess of bromine alone; greenish black products are thus obtained which appear to be perbromides of bromindigos; treatment of these bodies with sodium bisulphite removes the loosely combined bromine, giving the brominated dyes. Similar perbromides are obtained by using excess of bromine in presence of concentrated sulphuric acid (English Patent, 25,514, 1907).

The above-described processes—bromination in sulphuric or chloresulphonic acid, or with bromine alone—can also be applied to produce **penta- and hexa-bromindigos** (English Patents, 13,789, 1908; 2,609, 1909; 3,019, 1909), which also dye greenish blue shades.

According to Grandmougin (*Ber.*, 43, p. 937) the penta- and hexabromindigos obtained by bromination in sulphuric acid are the 4 : 5 : 7 : 5' : 7' and 4 : 5 : 7 : 4' : 5' : 7' bodies respectively.

An interesting process is that of Kalb in which dehydroindigo forms the starting point (*Ber.*, 42, p. 3642 *et seq.*, p. 3653 *et seq.*; B.A.S.F., English Patents, 16,377, 1909; 22,714, 1909).

**Dehydroindigo**, , is obtained by careful oxidation of indigo, for instance by means of silver oxide, lead dioxide, manganese dioxide, or

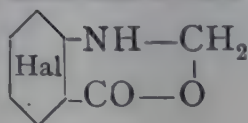
\* The trade names are here given on the authority of Bohn, *Ber.*, 43, p. 987.



permanganates, in absence of water, and in presence of indifferent diluents, e.g., chloroform, benzene, or nitrobenzene. If anhydrous acids are also present the corresponding dehydroindigo salts are formed. Dehydroindigo is also formed by treating indigo with halogen or halogenising agents under suitable conditions. With sodium sulphite or bisulphite, dehydroindigo forms soluble compounds, which can be readily halogenised by treatment with chlorine or bromine, even in presence of water; the tetrahalogen bodies thus produced are the 5:7:5':7' bodies. The other salts of dehydroindigo can be halogenised similarly; on reduction they yield the halogenindigos.

The unsymmetrical condensation product from isatin and indoxyl, indirubin, has been brominated by various processes; mono- to hexa-brom derivatives, dyeing reddish blue shades, have thus been obtained (S.C.I.B., English Patents, 6,106, 1907; 8,530, 1908; 6,351, 1910). The **tetra-bromindirubin** is known as **Ciba Heliotrope**.

Under the second method we may note two processes of the B.A.S.F. (English Patents, 6,991, 1909, and 6,992, 1909). According to the first of these a halogenised anthranilic acid is treated with formaldehyde, giving a compound of

the formula ; this on treatment with a cyanide gives the corre-

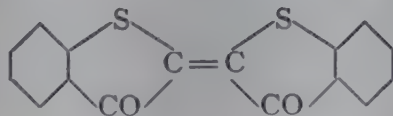
sponding  $\omega$ -cyanmethylantrānilic acid, , which is saponified to

halogenphenylglycine-*o*-carboxylic acid, for instance 3:4-, 4:5-, and 4:6-dihalogen-phenylglycine-*o*-carboxylic acid. The 4:6-dichlorophenylglycine-*o*-carboxylic acid thus prepared is identical with that prepared by chlorinating phenylglycine-*o*-carboxylic acid (English Patent, 20,552, 1901), and the tetrachlorindigo of this last-mentioned Patent is, therefore, the 5:7:5':7' body. According to the second Patent, No. 6,992, 1909, dihalogenphenylglycine-*o*-carboxylic esters are used as parent materials; by this process the 5:7:5':7'-, 4:5:4':5'-, 4:4':6:6'-, and 5:5':6:6'-tetrachlorindigos and the 4:4'-dichlor-5:5'-dibrom- and 5:5'-dichlor-7:7'-dibromindigos have been prepared.

In connection with the halogenindigos it is noteworthy that the ancient **Tyrian purple** obtained from *Murex Brandaris* has been shown by Friedländer (*Ber.*, 42, p. 765) to consist essentially of 6:6'-dibromindigo.

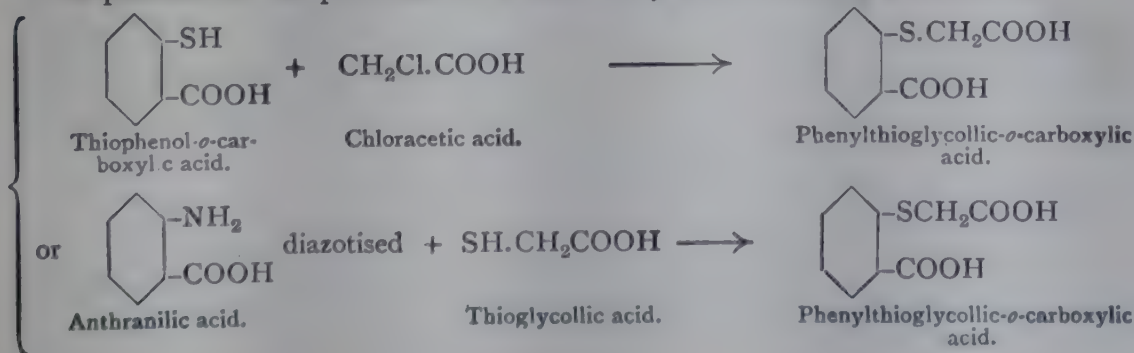
### Thioindigo Dyes

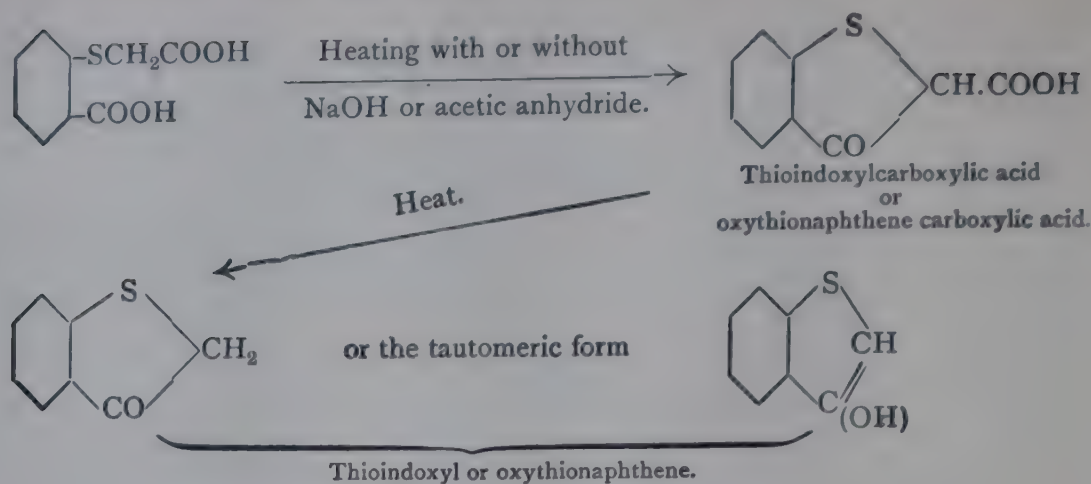
**Thioindigo** is an analogue of indigo containing sulphur in place of the NH groups—



It was discovered by Friedländer (*Ber.*, 39, p. 1060) and first put on the market as Thioindigo Red B by Kalle & Co. (English Patents, 22,736, 1905; 23,316, 1905; 14,261, 1906; 16,100, 1906; 16,101, 1906).

The process for its production is shown by the following scheme:—





Condensation and oxidation of this latter body gives thioindigo.

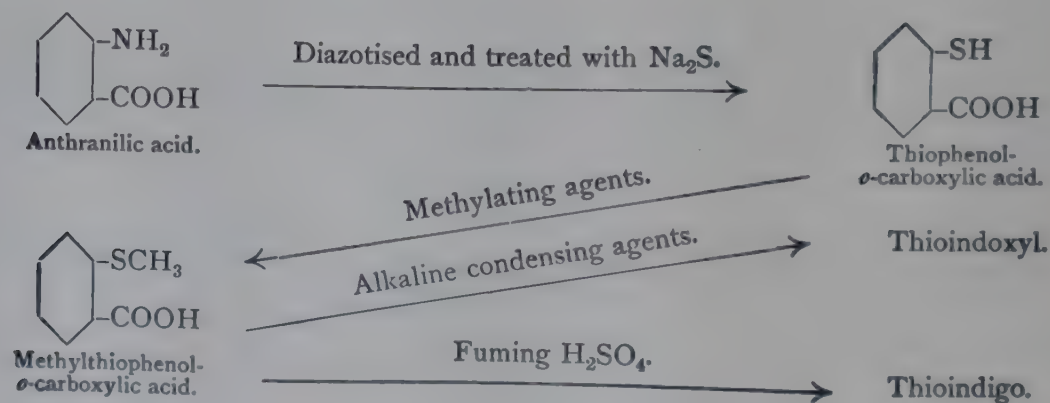
It will be seen that this process corresponds with the Heumann synthesis of indigo from phenylglycine-*o*-carboxylic acid.

This synthesis has been followed by the production of a large number of derivatives of thioindigo and allied dyes. The following general methods may be noted :—

2. Treatment of arylthioglycolic acids or their salts or esters,  $\text{RSCH}_2\text{COOR}_1$ , with acid condensing agents, such as sulphuric acid, phosphorus pentoxide, acetic anhydride, zinc chloride, potassium bisulphate, or oxalic acid, and oxidation of the resulting thioindoxyl derivatives (B.A.S.F., English Patent, 28,578, 1906).

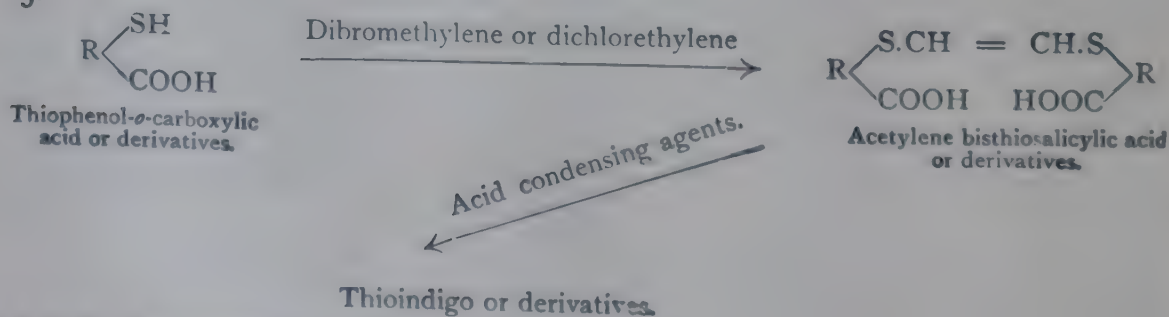
3. Conversion of arylthioglycolic acids into the acid chlorides,  $\text{RSCH}_2\text{COCl}$ , by means of phosphorus tri- or pentachloride or oxychloride; the acid chlorides on treatment with aluminium chloride give thioindoxyl derivatives (B.A.S.F., English Patent, 14,191, 1906).

4-



(F. v. M.L.B., English Patent, 593, 1907.)

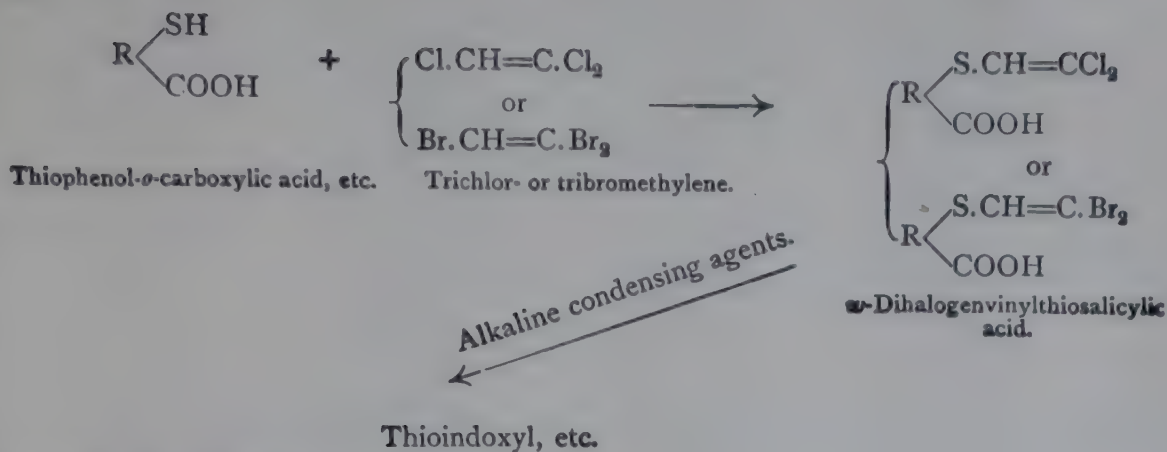
5.



(B.A.S.F., English Patent, 26,053, 1907.)

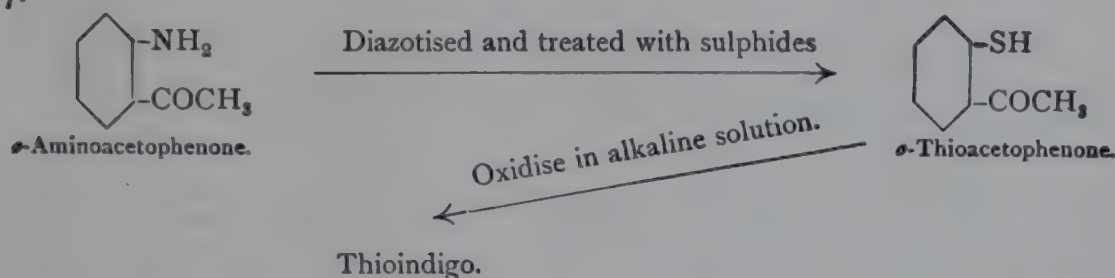


6.



(B.A.S.F., English Patent, 90, 1908.)

7.



(F. v. M.L.B., English Patent, 4,541, 1908.)

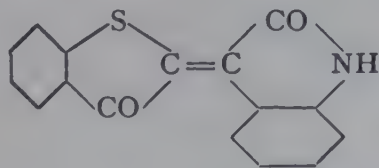
Among the derivatives of thioindigo we may note the following: Halogen derivatives obtained from halogenised parent materials or by halogenising the dyes, as in the case of indigo (S.C.I.B., English Patent, 6,490, 1907); alkyloxy and alkylthio derivatives (F. v. M.L.B., English Patent, 1,472, 1907); amino derivatives (F. v. M.L.B., English Patent, 16,584, 1907). The *m*-amino

compound  $\left( \text{H}_2\text{N}-\text{C}_6\text{H}_3(\text{CO})_2\text{S}-\text{C}=\text{C}-\text{S}-\text{C}_6\text{H}_3(\text{CO})_2-\text{NH}_2 \right)$  dyes brown shades, and the

*p*-amino compound  $\left( \text{H}_2\text{N}-\text{C}_6\text{H}_4(\text{CO})_2\text{S}-\text{C}=\text{C}-\text{S}-\text{C}_6\text{H}_4(\text{CO})_2-\text{NH}_2 \right)$  black shades; their

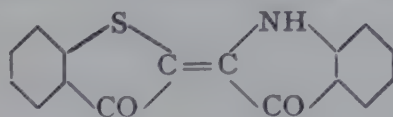
halogen derivatives dye orange and black shades respectively.

Unsymmetrical dyes containing only one thionaphthene residue have also been prepared. The condensation of thioindoxyl with isatin gives **Thioindigo Scarlet R**, the analogue of indirubin—



(Kalle, English Patent, 17,162, 1906.)

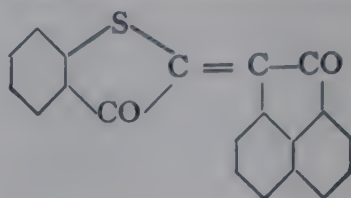
Condensation of thioindoxyl with  $\alpha$ -isatinanilide gives **Ciba Violet A**—



(S.C.I.B., English Patent, 11,760, 1906.)

The same product is obtained from  $\alpha$ -isatin chloride and thioindoxyl (Kalle, English Patent, 11,609, 1907.)

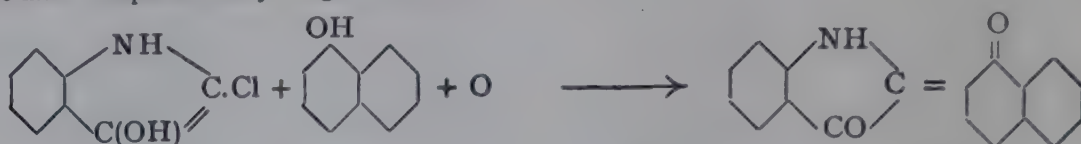
Condensation of thioindoxyl with acenaphthenequinone gives **Ciba Scarlet G**—



(S.C.I.B., English Patent, 344, 1908.)

### Other Indigoid Dyes

Friedländer (*Ber.*, 41, p. 772) has described dyes which contain half the indigo molecule, and may be termed indigoid dyes. They are obtained by condensing  $\alpha$ -isatin derivatives with phenolic compounds such as 1-naphthol, 1-anthrol, or their derivatives. The reactions between  $\alpha$ -isatin chloride and 1-naphthol may be given thus—



See also for these dyes, English Patents, 7,819, 1909 (Bayer); 3,206, 1910 (Kalle).

## 4. DI- AND TRIARYLMETHANE DYES

Under this heading are grouped a number of dyes, which may be regarded as derivatives of diphenylmethane and triphenylmethane—

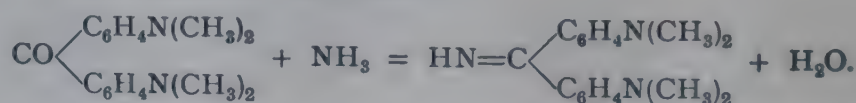


One or more of the phenyl groups may be replaced by naphthyl groups to give, e.g., diphenylnaphthylmethane dyes.

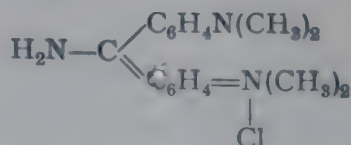
### (a) Diphenylmethane Dyes

The only important dyes of this class are the **Auramines**.

**Auramine** is obtained by treating tetramethyldiaminobenzophenone with ammonia; the reaction may be expressed:—



This represents the dye base as an imide; the dye is employed in the form of its hydrochloride, which may be formulated either as the hydrochloride of the imide base, or as—



Auramine may also be obtained by treating tetramethyldiaminodiphenylmethane,  $\text{CH}_2 \begin{cases} \text{C}_6\text{H}_4\text{N}(\text{CH}_3)_2 \\ \text{C}_6\text{H}_4\text{N}(\text{CH}_3)_2 \end{cases}$ , with sulphuric acid and then with ammonia.

The parent materials, tetramethyldiaminobenzophenone and tetramethyldiaminodiphenylmethane, are prepared by the action of phosgene and formaldehyde, respectively, on dimethylaniline (see pp. 434, 467).



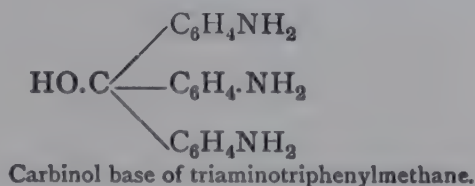
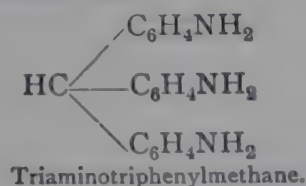
Auramine dyes wool, silk, or tannin-mordanted cotton bright yellow shades.

Auramine G is prepared similarly from dimethyldiaminoditolylmethane.

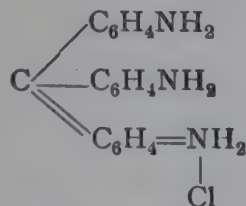
### (b) Triphenylmethane Dyes

These may be divided broadly into two types: (1) those containing amino groups; (2) those containing hydroxy groups, with or without carboxylic groups. The first of these, which is the more important, may again be subdivided into dyes containing two amino groups (Malachite Green type) and dyes containing three amino groups (Rosaniline type).

Before discussing the individual dyes of these groups, it will be well to consider generally their constitution. There are three stages to be considered in the formation of the amino dyes—the leuco base, the carbinol base, and the dye itself. The leuco bases are the triphenylmethane derivatives—thus Paraleucaniline, the leuco base of Pararosaniline, is triaminotriphenylmethane; oxidation of this body gives the carbinol base—



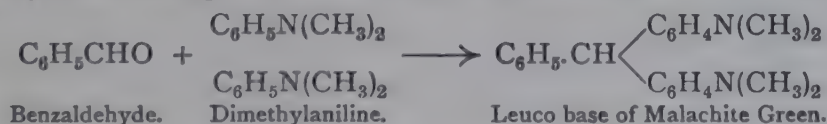
The dye **Pararosaniline** is the hydrochloride of this body, less the elements of water. Several formulæ are possible for such a body, and there has been considerable controversy as to the correct one. The balance of evidence appears to favour Nietzki's formula representing this body as quinonoid—\*



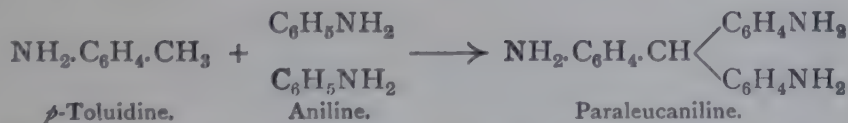
It should be noted that both the leuco base and the carbinol base are colourless—it is only when the carbinol base is converted into a salt that the dye results.

### General Methods of Production

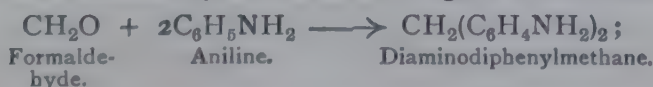
Triphenylmethane derivatives may be produced by a variety of processes. In each of these some compound must be present which will supply the methane carbon. Thus, for instance, benzaldehyde condenses with two molecules of dimethylaniline giving tetramethyldiaminodiphenylmethane, the leuco base of **Malachite Green**—



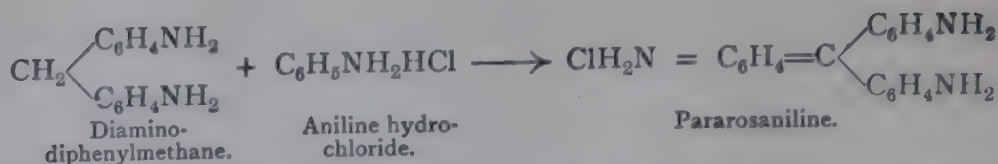
Or a methyl group attached to an aromatic nucleus may supply the methane carbon as in the production of Paraleucaniline (*v. supra*) by oxidising a mixture of *p*-toluidine and aniline:—



In the "New Fuchsine" process formaldehyde is employed. This condenses with two molecules of aniline to form diaminodiphenylmethane, which is then oxidised together with aniline and aniline hydrochloride to give Pararosaniline—



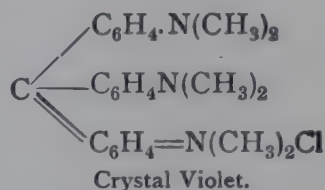
\* For a summary of the evidence see Sidgwick's "Organic Chemistry of Nitrogen," Oxford, 1910, p. 61.



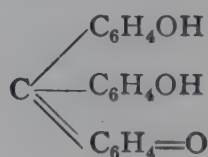
Phosgene, again, reacts with dimethylaniline to give tetramethyldiaminobenzophenone—



This may be converted into the chloride and condensed with a further molecule of dimethylaniline, or reduced to the benzhydrol, which is condensed with dimethylaniline and the leuco compound oxidised, giving **Crystal Violet**, hexamethyl pararosaniline hydrochloride—



Oxalic acid has also been employed, as in the manufacture of **Aurine** (tri-oxytriphenylcarbinol anhydride) from phenol, oxalic acid, and sulphuric acid. We may suppose that formic acid is first produced, which then reacts with the phenol, giving **Aurine**—



The preparation and properties of some typical triphenylmethane dyes are given below :—

### Diamino Compounds (Malachite Green Series).

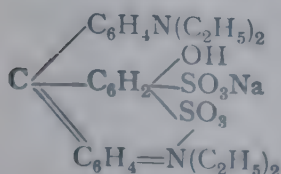
**Malachite Green** is essentially a salt of tetramethyldiaminotriphenyl carbinol. It usually appears in commerce as the zinc or iron double chloride, or the oxalate. Its method of preparation has already been indicated. It dyes wool, silk, and tannin-mordanted cotton green.

**Brilliant Green** is prepared similarly from benzaldehyde and diethylaniline; its dyeing properties are similar to those of Malachite Green.

**Setoglaurine** is prepared from *o*-chlorbenzaldehyde and dimethylaniline.

**Setocyanine**, **Victoria Green 3B**, and **Glacier Blue** are other dyes of this type.

The above-described dyes are basic dyes; the sulphonic acids of this series are acid wool dyes. Examples are **Erioglaurine A**, from benzaldehyde-*o*-sulphonic acid and ethylbenzylaniline sulphonic acid, **Night Blue B**, from *o*-chlor-*m*-nitrobenzaldehyde and ethylbenzylaniline sulphonic acid;

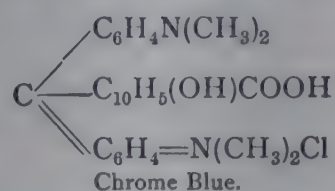
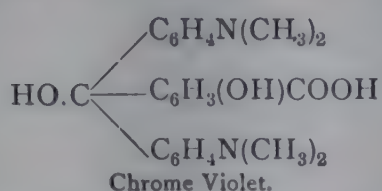
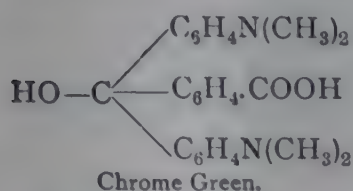


**Patent Blue V** is obtained by condensing *m*-oxybenzaldehyde with diethylaniline and sulphonating the product, or from *m*-nitrobenzaldehyde and diethylaniline, reducing and diazotising to form the hydroxy group, and sulphonating.

**Patent Blue A** is the corresponding product from ethylbenzylaniline.



The mordant dyes, **Chrome Green**, **Chrome Violet**, and **Chrome Blue**,

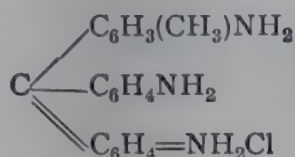


are obtained from tetramethyldiaminobenzhydrol and benzoic, salicylic, or  $\alpha$ -oxynaphthoic acid respectively, and may also be included in this class.

### Triamino Compounds—Rosaniline Series.

**Pararosaniline** (Parafuchsine, Paramagenta) has already been referred to (pp. 467, 468).

**Rosaniline** (Fuchsine, Magenta) is the hydrochloride of triaminodiphenyltolylcarbinol—



and is prepared similarly either by oxidising a mixture of aniline and *o*- and *p*-toluidine by various oxidising agents, or by the New Fuchsine process from formaldehyde, aniline, and *o*-toluidine. **New Fuchsine** (hydrochloride of triaminotritolylcarbinol) is prepared from formaldehyde and *o*-toluidine.

These three dyes are basic dyes, dyeing wool, silk, and tannin-mordanted cotton red shades.

Rosaniline is one of the oldest synthetic dyes, having been put on the market in 1859 by Verguin. The constitution of this and Pararosaniline was not, however, ascertained until 1878 by E. and O. Fischer (see for example Georgevics, "Chemistry of Dyestuffs," p. 137). The alkylated, benzylated, and arylated rosaniline dyes are also basic dyes; they are obtained either by alkylating, etc., the rosanilines or by treating the corresponding tertiary amines according to the general processes indicated above. Examples are:—

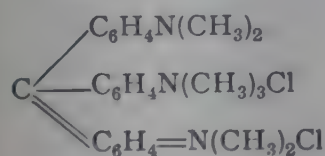
**Hofmann Violet**, a mixture of mono-, di-, and tri-methyl or -ethyl rosaniline and pararosaniline hydrochloride, from methyl or ethyl halides and rosaniline and pararosaniline.

**Aniline Blue**, spirit soluble, triphenylosaniline and triphenyl-pararosaniline hydrochloride, by the action of aniline on impure rosaniline.

**Methyl Violet**, penta- and hexa-methyl-pararosaniline, by the oxidation of dimethylaniline.

**Crystal Violet**, from dimethylaniline (*v.* above).

**Ethyl Violet**, the corresponding dye from diethylaniline.



**Methyl Green**, heptamethylpararosaniline chloride, by acting on Methyl Violet with methyl chloride.

**Ethyl Green**, ethylhexamethyl pararosanilinechlorbromide, by treating Methyl Violet with ethyl bromide.

**Benzyl Violet**, obtained by acting on Methyl Violet with benzyl chloride.

The sulphonic acids of the rosaniline series are obtained either by sulphonating the basic dyes, or from the amine sulphonic acids. Typical examples are:—

**Acid Magenta**, a mixture of trisulphonic acids of rosaniline and pararosaniline obtained by sulphonation of the bases, dyes wool in acid baths.

**Alkali Blue**, monosulphonic acid of triphenylosaniline and triphenylpararosaniline, obtained by sulphonation, dyes wool in an alkaline bath.

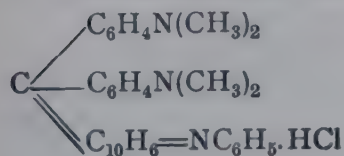
**Soluble Blue** is the corresponding trisulphonic acid, and dyes silk and mordanted cotton.

**Höchst New Blue**, a trisulphonic acid obtained by sulphonation of trimethyltriphenylpararosaniline (obtained from phosgene and methyldiphenylamine), dyes wool from acid baths.

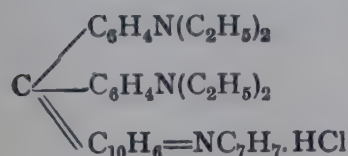
**Acid Violet 6B**, disulphonic acid of dimethyldiethyldibenzyltriaminotriphenylcarbinol, obtained from dimethyl-*p*-aminobenzaldehyde and ethylbenzylaniline sulphonic acid, dyes wool from acid baths.

**Eriocyanine A**, tetramethyldibenzylrosanilinedisulphonic acid, from tetramethyldiaminobenzhydrol sulphonic acid and dibenzylaniline sulphonic acid, dyes wool reddish blue in acid baths.

We may include here the triaminodiphenylnaphthylmethane dyes:—



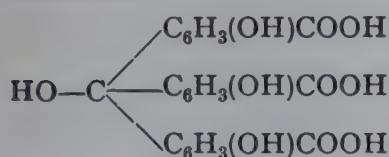
**Victoria Blue B** is obtained from phenyl- $\alpha$ -naphthylamine and tetramethyldiaminobenzophenone chloride or tetramethyldiaminobenzhydrol. It dyes wool, silk, or cotton from acid baths, or mordanted cotton.



**Night Blue** is similarly obtained from *p*-tolyl- $\alpha$ -naphthylamine, and has similar dyeing properties.

### Hydroxy Compounds—Aurine Series

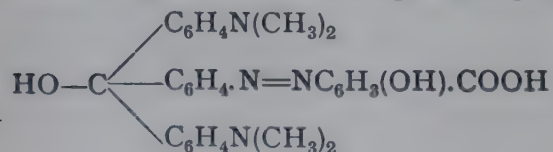
**Aurine**, rosolic acid, has already been referred to; it is used for colouring varnishes.



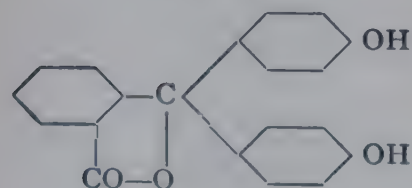
**Chrome Violet**, aurine tricarboxylic acid, is obtained from formaldehyde and salicylic acid; used for printing chrome mordanted cotton.

A number of mordant dyes of this series have been prepared recently; see English Patents, 15,204, 1907 (Geigy); 14,311, 1909; 14,312, 1909; 368, 1910; 1,411, 1910; 6,364, 1910 (Bayer); 12,130, 1910; 17,087, 1910 (M.L.B.).

We may finally note the azotriphenylmethane dyes, one of which, **Alizarin Yellow F.S.**, has already been referred to under azo dyes. They are obtained from triphenylmethane dyes containing free amino groups by diazotising and coupling with components and oxidising. For example—



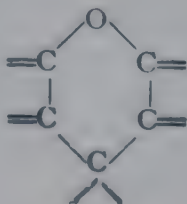
**Azo Green** is obtained from diazotised *m*-aminotetramethyldiaminotriphenylmethane and salicylic acid; dyes chromed wool.



**Phenolphthalein**, the lactone of dioxytriphenylcarbinolcarboxylic acid, obtained from phenol and phthalic anhydride, may be classed in the aurine series, though its production is analogous to that of the phthaleins (*q.v.*); it is employed as an indicator in volumetric analysis.

### 5. PYRONE DYES

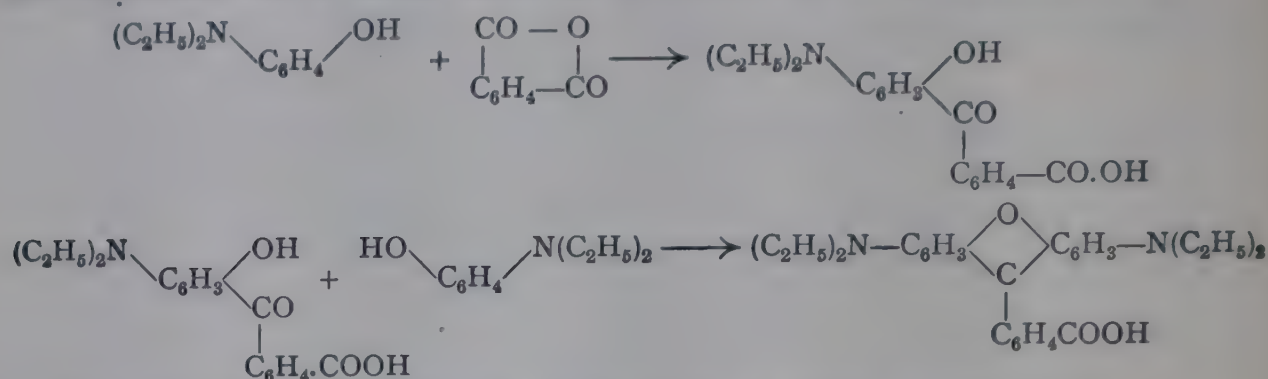
The dyes of this class are closely allied to the di- and tri-phenylmethane dyes, and are sometimes classed with them. It is more convenient, however, to treat them as a separate group and to regard them as pyrone or xanthene derivatives. They all contain the pyrone ring—







anhydride, or by condensing equimolecular proportions of diethyl-*m*-aminophenol and phthalic anhydride to form diethyl-*p*-amino-*o*-oxybenzoylbenzoic acid, which is then condensed with a further molecular proportion of diethyl-*m*-aminophenol.



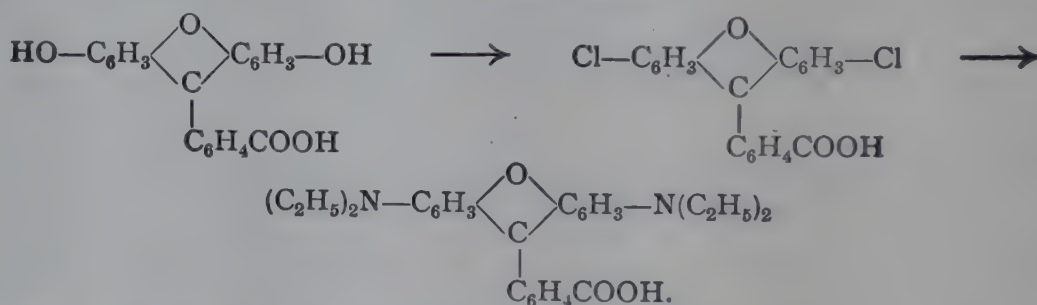
By this second method unsymmetrical rhodamines can be obtained, for example :—

**Rhodine 2G** from dimethylaminooxybenzoylbenzoic acid and ethyl-*m*-aminophenol, the carboxylic group of the dye being finally converted into its ethyl ester.

**Rhodamine 12GM**, from dimethylaminooxybenzoylbenzoic acid and resorcinmethyl ester, and esterification of the product.

**Irisamine G**, from dimethylaminooxybenzoylbenzoic acid and *m*-amino-*p*-cresol, the product being esterified.

**Rhodamine B** can also be obtained by converting fluorescein into its chloride by  $\text{PCl}_5$ , and treating the chloride with diethylamine :—



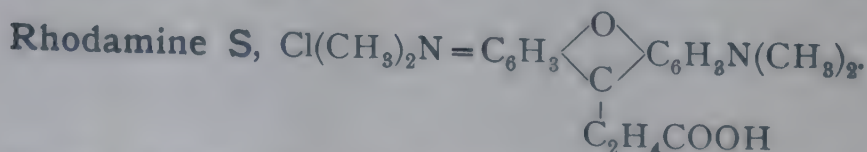
By applying this method the corresponding arylaminoxanthene derivatives can be produced, the sulphonic acids of which are acid wool dyes (whereas the Rhodamines described above are basic dyes, dyeing tanned cotton, wool, or silk various shades of red).

Examples of such acid dyes are :—

**Fast Acid Violet B** (Violamine B),  $\text{C}_6\text{H}_5\text{N}=\text{C}_6\text{H}_3-\begin{array}{c} \text{O} \\ \diagup \quad \diagdown \\ \text{C} \quad \text{C} \\ | \quad | \\ \text{C}_6\text{H}_4\text{COONa} \end{array}-\text{C}_6\text{H}_3-\text{NH}\cdot\text{C}_6\text{H}_4\text{SO}_3\text{Na}$ , obtained by sulphonating the product of reaction of aniline on fluorescein chloride.

**Fast Acid Violet A2R** (Violamine R), and **Violamine G**, are the corresponding sulphonic acids obtained by sulphonation of the products from *o*-toluidine and *p*-phenetidine respectively.

The above derivatives of phthalic acid are known as **Phthaleins**; succinic anhydride gives similar products known as **Succineins**. For example :—

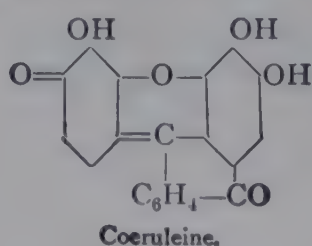
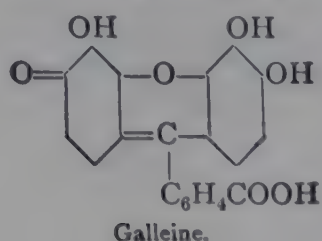


Finally, mention should be made of two phthaleins of somewhat different properties, viz. :—

**Galleine** from gallic acid or pyrogallol and phthalic anhydride, a violet mordant

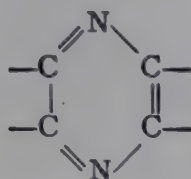


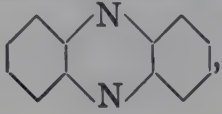
dye, and **Caeruleine**, an anthracene derivative, obtained by treating galleine with concentrated sulphuric acid; a green mordant dye:—

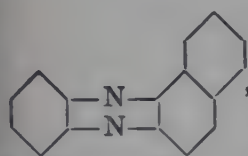


## 6. AZINE DYES

The azines are characterised by containing the azine (pyrazine, paradiazine) ring:—

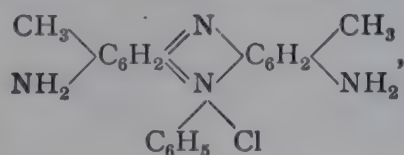


The azine dyes of the anthracene series (indanthrene, etc.) have already been described. We shall consider here those azines which contain other aromatic nuclei. The simple azines, like diphenazine, , or naphthophenazine,



like the simple azo compounds, are not dyes. But when the nuclei contain suitable substituents ("auxochromes"), such as  $\text{NH}_2$  or  $\text{OH}$ , the products are in general dyes. It is now usual to formulate the azine dyes as possessing an ortho-quinonoid structure, and this practice will be followed in the succeeding pages.

In some cases, *e.g.*, the safranines, alkyl or aryl groups are attached to one of the two nitrogen atoms, which is then regarded as quinquevalent, the dyes being then referred to as azonium compounds,—*e.g.*, **Safranine T**—



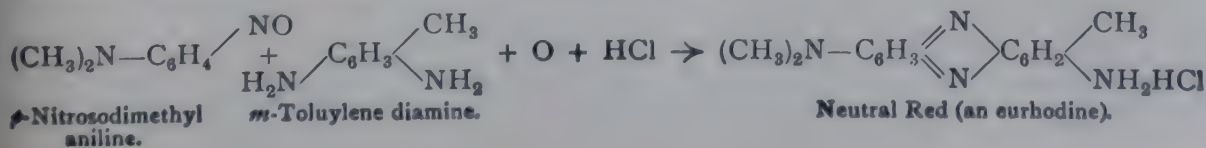
*i.e.*, meso-phenyldiaminoditolylazonium chloride, mixed with the corresponding meso-tolyl body.

The principal group of azines to be considered are the **Eurhodines**, the **Rosindulines** and **Isorosindulines**, the **Safranines**, and the **Indulines**.

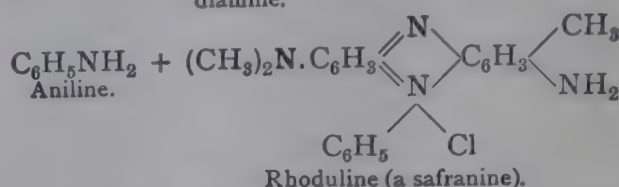
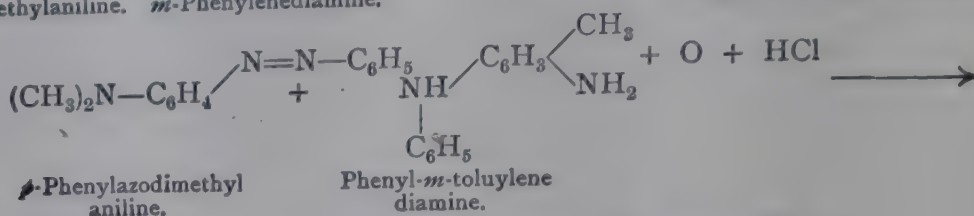
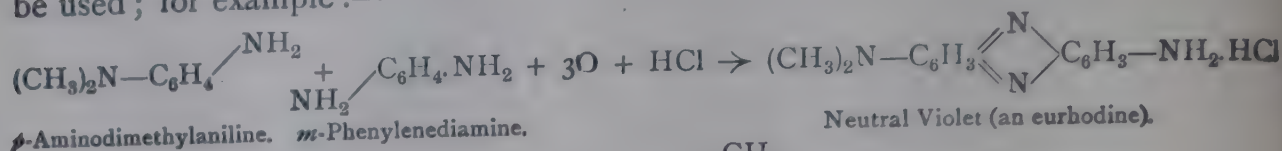
The **Eurhodines** are aminodiphenazines, the **Rosindulines** and **Isorosindulines** are naphthophenazine compounds, the **Safranines** are, as previously stated, meso-alkyl- or -aryl-diaminoazines, while the **Indulines** are meso-alkyl- or -aryl- tri- and -tetraaminoazines.

The following general methods for the production of azines should be noted:—

1. Condensation and Oxidation of a *p*-nitroso derivative of an amine with a second amine. For example:—

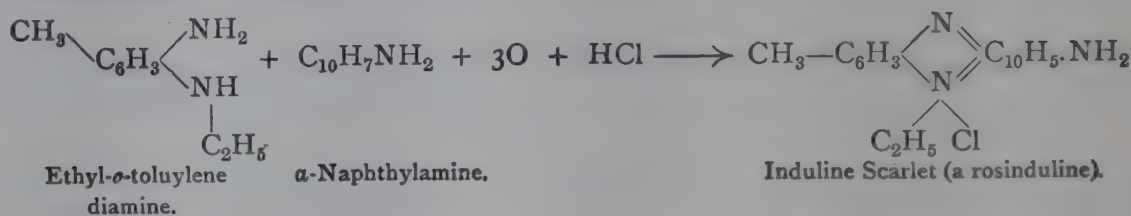


Instead of a *p*-nitroso compound, a *p*-diamine or a *p*-aminoazo compound may be used; for example:—

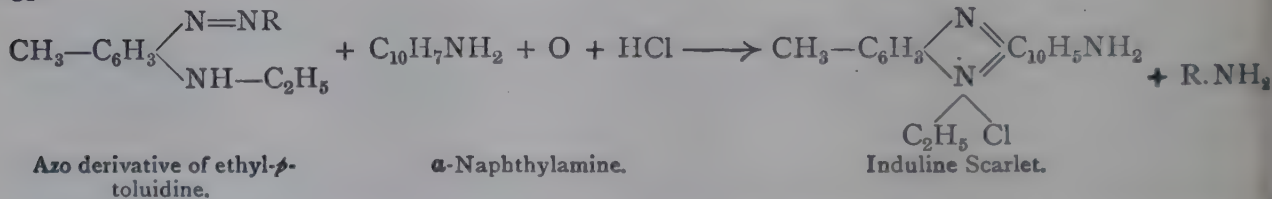


In the latter reaction it will be noted that the azo compound splits up and an amine forms as a bye-product.

2. Both the azine nitrogen atoms may be obtained from an *o*-diamine or *o*-aminoazo compound, *e.g.*:—

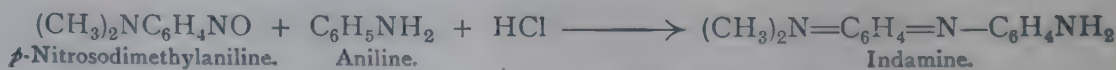


or

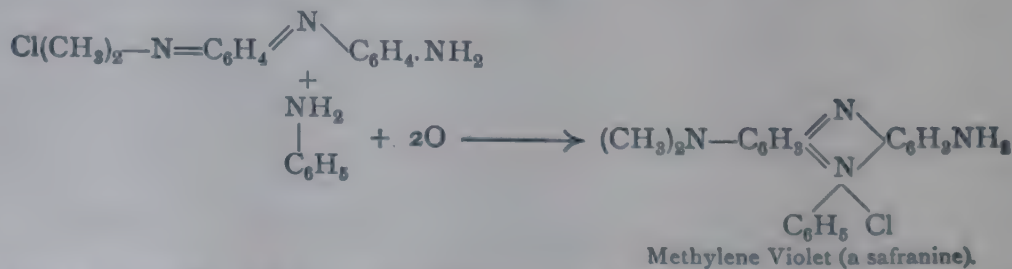


3. The most important method is that in which three components are used; this method is largely employed for obtaining Safranines.

Obviously this method is capable of yielding a great variety of products. The process may be carried out either in one step or two. If, for example, a *p*-nitroso compound of an amine is condensed with another amine, an intermediate product, an indamine, is formed, thus:—



The indamines are too unstable to be used for dyes, but on oxidation with another molecule of an amine give azines, *e.g.*:—

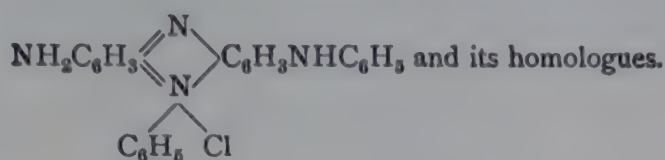


Obviously, instead of a *p*-nitroso compound a *p*-diamine or *p*-aminoazo compound may be used.

The three components may be directly condensed and oxidised to the azine without isolation of an intermediate indamine. This was the method by which



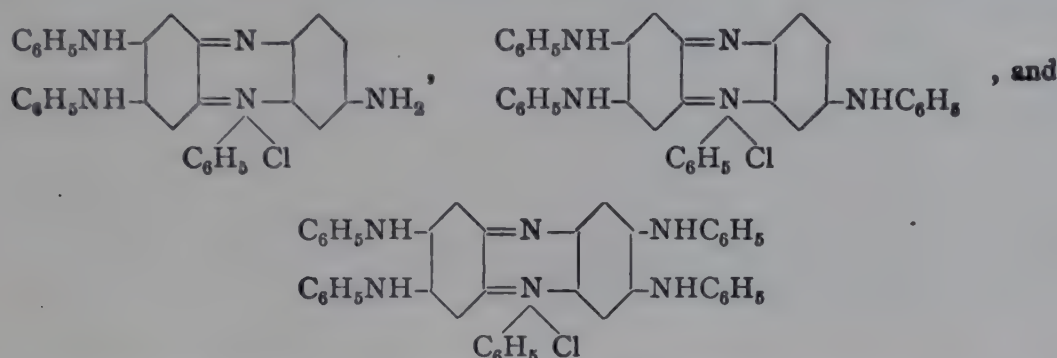
the first synthetic dye, **Mauveine**, was obtained by Perkin in 1856. Mauveine is a mixture of Safranines obtained by oxidising an impure aniline containing toluidine. It consists of—



**Safranine T**, previously referred to (p. 473), is obtained by this method from *p*-toluylene-diamine, analine, and *o*-toluidine, or *p*-toluidine and *o*-toluidine (two molecules.)

Similarly, **Phenosafranine**, mesophenyl-diaminophenazonium chloride, is obtained from *p*-phenylenediamine and two molecular proportions of aniline.

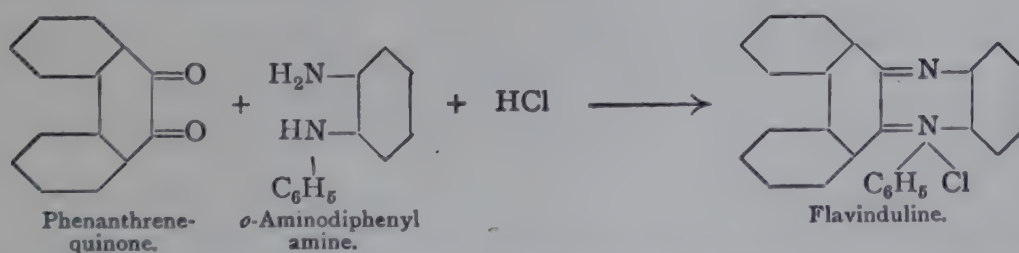
The indulines are produced by a similar method; **Induline** itself contains mesophenyl-dianilinoaminodiphenazonium chloride, and mesophenyl-tri- and -tetra-anilinophenazonium chloride:—



and is prepared by heating aminoazobenzene with aniline and aniline hydrochloride. Here arylamino groups are introduced into the molecule by means of the excess of aniline.

**Nigrosine** is similar in composition, and is prepared by heating aniline and its hydrochloride with nitrobenzene and a metal. These two dyes are principally used in the production of varnishes and inks (see p. 491).

4. Another method which is a direct condensation without oxidation, viz., condensation of an *o*-diamine with an *o*-quinone, is illustrated by the preparation of **Flavinduline**:—



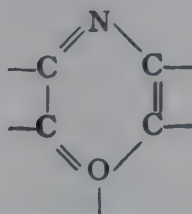
A large number of other azines are known, but the above are sufficiently typical and illustrate the general methods.

Those azines which contain only amino groups are in general basic dyes, dyeing tannin-mordanted cotton or silk usually red, violet, or blue shades. When sulphonic acid groups are present, *i.e.*, when the dyes are derived from sulphonated parent materials, or are sulphonated after their production, the products are acid wool dyes; practically the only recent developments in the azine series are in the production of acid wool dyes of the Safranine type.

We may note finally that some azo dyes have been prepared by diazotising azine dyes containing amino groups and coupling with  $\beta$ -naphthol, etc.; **Indoin Blue** (diazotised Safranine T +  $\beta$ -naphthol) is an example.

## 7. OXAZINE DYES

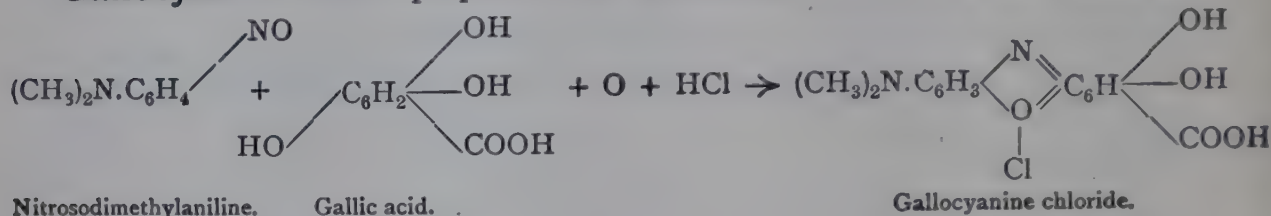
The oxazine dyes are analogous to the azines, but contain, instead of the azine ring, the oxazine ring:—



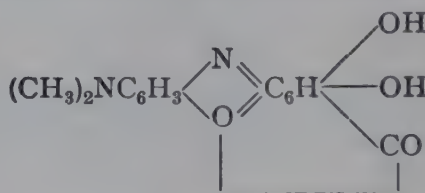
The oxazines are usually formulated as ortho-quinonoid compounds. It will be seen from the examples given below that the general methods of preparation are analogous to those employed in the production of the azines.

The most important group of oxazines is the **Gallocyanines**, which are obtained from gallic acid and its derivatives, and are employed for producing blue shades by printing on cotton or wool with chrome mordants.

**Gallocyanine** itself is prepared from nitrosodimethylaniline and gallic acid:—



The free base may be formulated as the anhydride:—

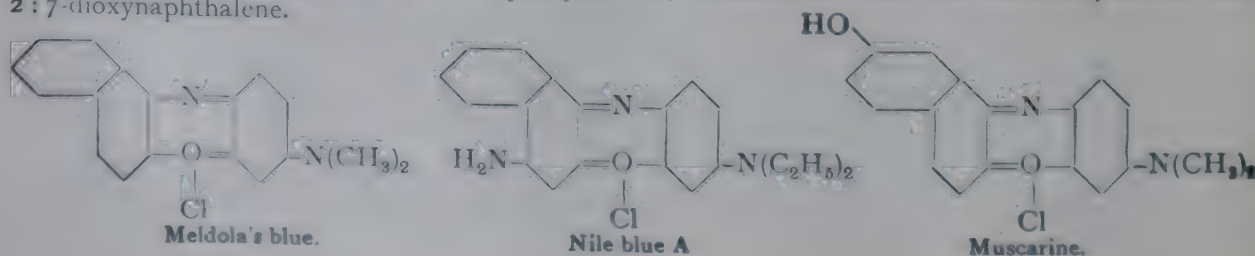


By using derivatives of gallic acid other gallocyanines are produced, *e.g.*, **Prune**, from nitrosodimethylaniline and methylgallate; **Gallamine Blue**, from nitrosodimethylaniline and gallamide; **Celestine Blue B**, from nitrosodiethylaniline and gallamide. In these processes the *p*-aminoazo compounds can be used instead of the *p*-nitroso bodies (*cf.* the corresponding processes for preparing azines).

Reduction converts the gallocyanines into their leuco derivatives (**1900 Blue**, **Modern Violet**, etc.), which for some purposes are preferable to the parent dyes. The action of bisulphites also give products which are probably modified leuco derivatives. Gallocyanines can be condensed with aromatic amines or phenols; for example, **Delphine Blue** is prepared by condensing gallocyanine with aniline and sulphonating the product, while **Phenocyanine VS** is obtained from diethylgallocyanine and resorcin. By heating ordinary gallocyanine in solution or suspension in an acid, neutral or alkaline medium, CO<sub>2</sub> splits off and a pyrogallol-gallocyanine is obtained (see English Patents, 20,802, 1906; 9,961, 1907; 1,334, 1908).

The other oxazine dyes need not be discussed at length. Examples are:—

**Meldola's Blue** (New Blue), from nitrosodimethylaniline and  $\beta$ -naphthol; **Nile Blue A**, from nitrosodiethyl-*m*-aminophenol and  $\alpha$ -naphthylamine; **Muscarine**, from nitrosodimethylaniline and 2:7-dioxynaphthalene.

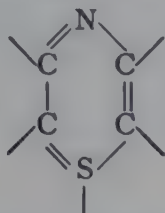




## 8. THIAZINE, THIAZOLE, AND SULPHIDE DYES

These three groups of dyes are conveniently considered together, as they are each characterised by containing sulphur, in a ring or otherwise.

The **Thiazines** contain the six-membered ring—



which may be compared with the azine and oxazine rings.

A typical thiazine is **Methylene Blue**, tetramethyldiaminodiphenazthionium chloride,  $(\text{CH}_3)_2\text{N} \cdot \text{C}_6\text{H}_3 \begin{smallmatrix} \text{N} \\ \diagup \text{S} \diagdown \\ \text{Cl} \end{smallmatrix} \text{C}_6\text{H}_3\text{N}(\text{CH}_3)_2$ . It is prepared by oxidising dimethyl-

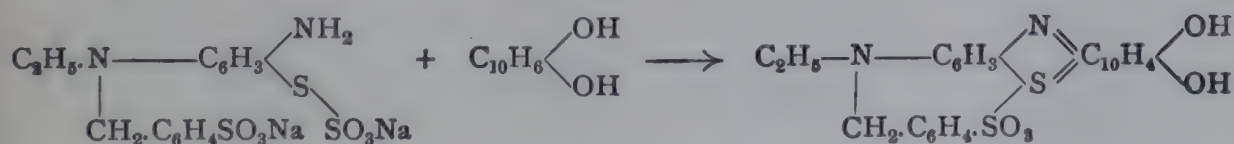
*p*-phenylenediamine together with sodium thiosulphate to give the thiosulphonic acid,  $(\text{CH}_3)_2\text{N} \cdot \text{C}_6\text{H}_3 \begin{smallmatrix} \text{NH}_2 \\ \diagup \text{S} \cdot \text{SO}_3\text{H} \end{smallmatrix}$ , which is then oxidised with dimethylaniline to the indamine,  $(\text{CH}_3)_2\text{N}=\text{C}_6\text{H}_3=\text{N}-\text{C}_6\text{H}_4-\text{N}(\text{CH}_3)_2$ , which, on further oxidation, gives

first **Leucomethylene Blue**,  $(\text{CH}_3)_2\text{N} \cdot \text{C}_6\text{H}_3 \begin{smallmatrix} \text{NH} \\ \diagup \text{S} \end{smallmatrix} \text{C}_6\text{H}_3-\text{N}(\text{CH}_3)_2$ , and then the dye.

Methylene blue is a basic dye, dyeing tannin-mordanted cotton. It has also therapeutic properties.

**New Methylene Blue N**, diethyldiaminotoluphenazthionium chloride, is obtained similarly from *p*-aminoethyl-*o*-toluidine, sodium thiosulphate, and ethyl-*o*-toluidine, and has similar properties.

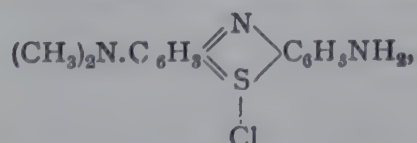
**Brilliant Alizarin Blue**, ethylbenzylaminophenodioxynaphthazthionium sulphonic acid anhydride, is obtained by oxidising *p*-aminoethylsulphobenzylaniline thiosulphonic acid and  $\beta$ -naphthohydroquinone:—



It dyes chromed wool, cotton, or silk.

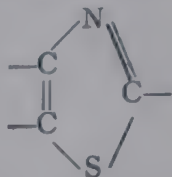
Another method of obtaining the thiazine ring consists of the use of sulphuretted hydrogen and ferric chloride; for example:—

**Gentianine**, dimethyldiaminodiphenazthionium chloride,

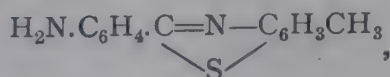


is obtained by oxidising by means of ferric chloride, *p*-phenylenediamine with dimethyl-*p*-phenylenediamine in presence of sulphuretted hydrogen.

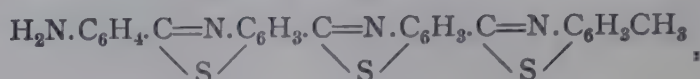
The **Thiazoles** contain the five-membered ring :—



The typical thiazole is **Primuline**, a yellow direct cotton dye ; it is obtained by heating *p*-toluidine with sulphur, whereby dehydrothiotoluidine,



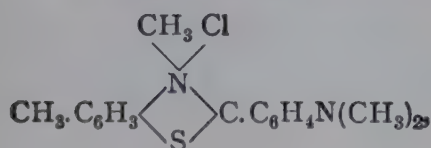
is first formed ; this, on further heating with sulphur, condenses to the primuline base :—



which is sulphonated to give Primuline.

As previously described, Primuline can be diazotised and combined with azo dye components, and it is used thus for producing azo dyes on the fibre (see **Developing Dyes**, p. 450).

Methylation of dehydrothiotoluidine gives **Thioflavine T**,



which dyes tannin-mordanted cotton or silk greenish yellow.

**The Sulphide Dyes** (p. 545) form a very large and important group. They are characterised in general by the property of dissolving in sodium sulphide solutions and dyeing cotton from such a bath. Some, however, are insoluble in sodium sulphide, but dissolve in alkali hydrosulphite and thus behave as vat dyes. The method of preparation is very simple, consisting in melting the parent substance with sulphur or more usually with sulphur and sodium sulphide. The parent substances used are very diverse. The first sulphide dyes were prepared from natural organic bodies, such as sawdust, bran, woodpulp, etc., and the product, **Cachou de Laval**, dyed cotton brown shades. The first sulphur dye from a synthetic organic compound was **Vidal Black** from *p*-aminophenol. A large number of sulphide dyes have been prepared from diphenylamine derivatives, *e.g.*, **Immedial Black V**, from dinitrooxydiphenylamine, **Immedial Sky Blue**, from diethyl-*p*-amino-*p*'-oxy-diphenylamine.

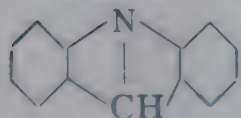
Cassella & Co. form indophenolic bodies by condensing *p*-nitrosophenol with carbazole or its N-alkyl, etc., derivatives; and then sulphurise. **Hydroin Blue R** and **G** (see English Patents, 2,918, 1909 ; 9,689, 1909 ; 14,143, 1909 ; 18,822, 1909 ; 22,138, 1910) are vat dyes of this type.

The sulphur dyes derived from anthraquinone have already been referred to (see **Anthracene Dyes**, p. 458).

Although so many sulphur dyes have been prepared, their constitution is not known with certainty. Probably many of them, for example, Immedial Sky Blue, contain a thiazine ring, and also contain a thio or dithio group (R.S.H. or R.S.S.R.).

## 9. ACRIDINE DYES

This is a small group of basic dyes, which contain the acridine nucleus,

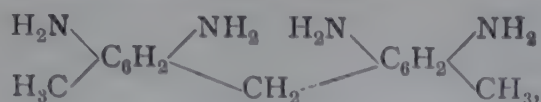


A typical method of preparation may be illustrated by the case of

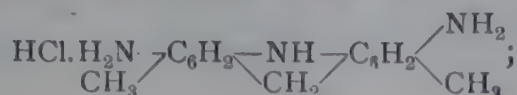
**Acridine Yellow**, diaminodimethylacridine ; condensation of formaldehyde with



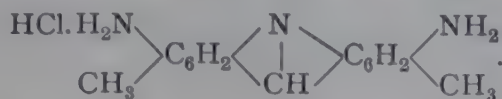
*m*-toluylenediamine gives tetraminoditolylmethane



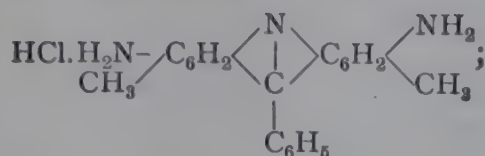
from which, on heating with acids, ammonia splits off, giving a hydroacridine derivative:



this on oxidation, say, with ferric chloride, gives the dye,

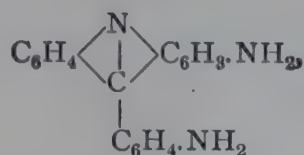


A similar condensation, using benzaldehyde and *m*-toluylenediamine, gives **Benzoflavine**, diaminodimethyl-meso-phenylacridine,

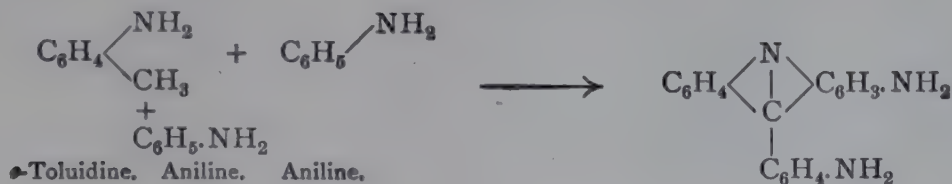


dyes yellow shades.

Another yellow acridine dye, which is used for dyeing leather, is **Phosphine**, a diaminophenylacridine,



first obtained as a by-product in the manufacture of Rosaniline. Its formation may be represented thus—



## 10. MINOR GROUPS OF DYES

A brief description will be given here of a number of small groups of dyes:—

(a) **Nitro Dyes**.—Some simple nitro compounds possess dyeing properties. Examples are: **Picric acid** (trinitrophenol), **Martius yellow** (dinitro- $\alpha$ -naphthol), **Naphthol yellow S** and **RS** (dinitronaphthol sulphonic acids), **Aurantia** (hexanitrodiphenylamine); all are acid wool dyes.

Picric acid is still used to some extent for silk and leather.

(b) **Nitroso-Phenol** or **Quinoneoxime Dyes**.—These are practically obsolete dyes; examples are **Fast Green O** (dinitrosoresorcin or benzoquinonedioxime), **Gambine R** and **Y** (nitrosonaphthols or naphthoquinoneoximes), **Dioxine** (nitrosodihydroxynaphthalene or hydroxynaphthoquinoneoxime); these are mordant dyes.

(c) **Quinoline Dyes**.—These are chiefly of interest because of the use of some of them in photography (see **Photographic Chemicals**, p. 655).

**Cyanine**, obtained by the action of amyl iodide on a mixture of quinoline and lepidine, and **Quinoline Red**, from benzotrichloride, quinoline, and isoquinoline, are examples of these.

**Quinoline Yellow**, quinophthalone, is obtained from quinaldine and phthalic anhydride; sulphonation of this product gives a soluble wool dye.

(d) **Oxyketone Dyes** (other than anthracene derivatives).—A few mordant dyes of this type may be noted. **Alizarin Yellow A**, trioxybenzophenone, from benzoic acid and pyrogallol; **Alizarin Yellow C**, trioxyacetophenone, from acetic acid and pyrogallol; **Galloflavine**, obtained by oxidising gallic acid; and **Alizarin Black S** or **Naphthazarine S**, the bisulphite compound of naphthazarine,

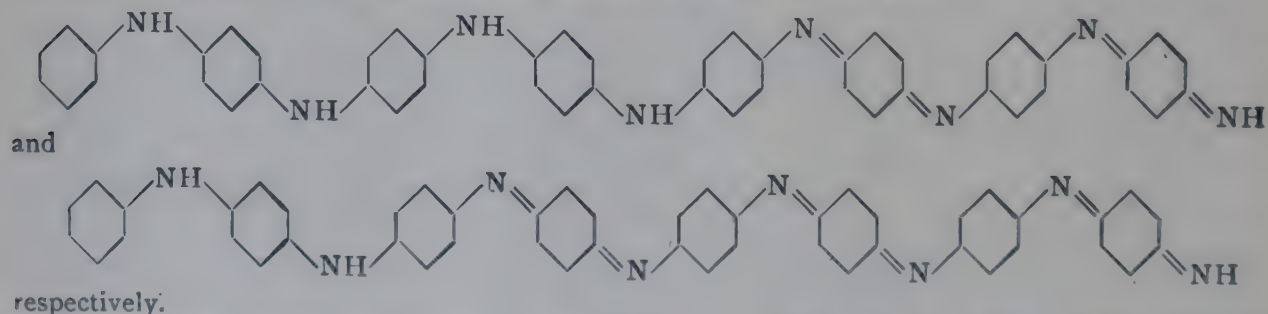


(e) **Indamines and Indophenols**.—These are compounds of the type  $\text{NH}_2\text{C}_6\text{H}_4\text{—N=C}_6\text{H}_4\text{=NH}$  and  $\text{NH}_2\text{C}_6\text{H}_4\text{—N=C}_6\text{H}_4\text{=O}$ , respectively. They are

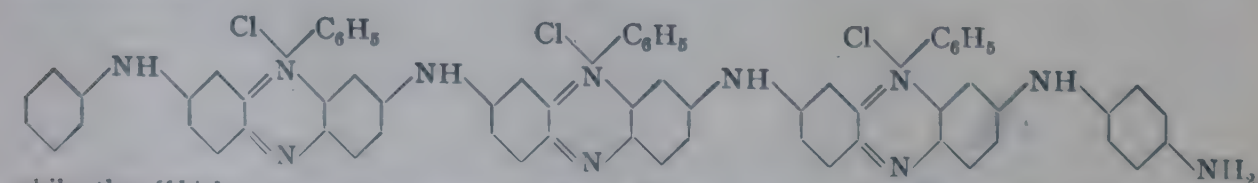
too unstable to be used as dyes; the production of indamines as intermediate products in the manufacture of azine and thiazine dyes has already been referred to (*q.v.*). On reduction they yield diphenylamine derivatives, and hence they are of importance as the parent materials for the manufacture of sulphur dyes.

(f) **Aniline Black**.—This old and still highly important dye should be more properly discussed under dyeing, since it is practically always formed on the fibre, by impregnating the material with aniline salts and oxidising by means of chlorates, etc. Many variations on the process have been suggested, chiefly with a view of obtaining a black which will not turn green. In order that the oxidation should proceed as desired, catalysts such as vanadium, copper and iron salts are used. Oxidation is carried out at an elevated temperature.

The constitution of aniline black has been the subject of many researches. It has the empirical formula  $(\text{C}_6\text{H}_5\text{N})_x$ . According to Green and Woodhead (*Journ. Chemical Society*, 1910, p. 2388), a series of quinonoid bodies containing eight nuclei can be obtained by oxidation of aniline, viz., proto-emeraldine, emeraldine, nigraniline, and pernigraniline, the first and last of these being unstable bodies; aniline blacks prepared in substance consist of a mixture of emeraldine, nigraniline, and higher condensation products, while the blacks produced on the fibre consist largely of higher condensation products. **Emeraldine** and **nigraniline** are formulated as—



In subsequent publications (*Journ. Soc. Dyers*, 1913, pp. 105 *et seq.*, 338 *et seq.*), Green develops the view that his blacks are **azonium** compounds, obtained by conjoint oxidation of products of the emeraldine series with a further amount of aniline; the “aged” and “chlorate” blacks are formulated as—



while the “bichromate” blacks are regarded as the corresponding hydroxy compounds (*cf.* English Patent, 19,124, 1912).

**For Dyeing Processes with Aniline Black** (see pp. 544, 556, 557).



## SECTION XIV

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### The Industry of Natural Dye-Stuffs





# THE INDUSTRY OF NATURAL DYE-STUFFS

BY G. MARTIN, Ph.D., D.Sc.

## LITERATURE

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THE natural colouring matters of animal and vegetable origin have been used for dyeing for hundreds, and in some cases for thousands, of years. Since the manufacture of the artificial colouring matters from coal-tar their use has enormously decreased. A few, however, still possess some importance, viz., indigo and logwood. Artificial indigo, however, is now being manufactured in large quantities, and no doubt in course of time the use of the natural colouring matters will entirely die out, being replaced by superior and cheaper synthetic products.

**Statistics.**—The following figures show the value of the natural dye-stuffs imported into the United Kingdom :—

	1906.	1910.	Value.
	Cwt.	Cwt.	
Cochineal - - - -	2,270	1,269	£7,321
Cutch - - - -	5,217	3,202	86,803
Natural indigo - - -	7,641	3,350	43,054
Logwood - - - -	359,820	217,340	42,000
Other dye woods - - -	70,360	104,360	38,755
Dye wood extracts were valued in 1908 at £176,318; in 1910 at £156,359.			

The United States imports were :—

	1906.	1910.	Value in 1910.
Cochineal - - - -	111,000 lbs.	151,000 lbs.	\$41,000
Cutch - - - -	...	28,000 „	1,278
Indigo (natural) - - -	193,000 lbs.	125,000 „	66,000
Annatto - - - -	...	619,372 „	40,000
Turmeric - - - -	...	...	28,000
Dye woods in a crude state—			
Fustic - - - -	...	5,800 tons	83,000
Logwood - - - -	37,000 tons	32,000 „	368,000
All other - - - -	...	923 „	33,000
Extracts—			
Logwood and other dyewoods	3,390,000 lbs.	3,270,000 lbs.	198,000
Persian berries - - -	...	83,000 „	8,000
Chlorophyll - - - -	...	4,000 „	3,000

For modern statistics see Appendix III.

## Black and Blue Colouring Matters

**Indigo** is treated under **Coal-tar Colours**, p. 459*d*.

**Logwood** \* (Campeachy wood, German, *Blauholz*, wood of *Hæmatoxylon campechianum* of Central America) contains a colouring matter termed **hæmo-**

\* See also pp. 490, 551, 552.

**toxylin**,  $C_{16}H_{14}O_6 + 3H_2O$  (yellow prisms, p. 490), which when oxidised is converted into the real colouring matter, hæmatein,  $C_{16}H_{12}O_6$ . This is soluble in alkalis giving a deep blue colour, and violet precipitates with aluminium salts, blue with copper, and black with iron and chromium. For dyeing purposes the wood in the form of sawdust or chips was formerly used, but now extracts are usually employed:

1. In the **American Method of extraction** the wood is extracted five times for fifteen minutes in autoclaves at 1-5 atmospheres pressure. The largest yield is thus obtained, but it contains impurities such as resin, tannic acid, sugar, etc., which influence the dyeing unfavourably.

2. In the **French Method** the extraction is made by simply boiling the wood under ordinary pressure, yielding a good and copious extract.

3. In the **Diffusion Method** the wood is extracted similar to the extraction of beets in the sugar industry. Yield small but of best quality, and therefore dear.

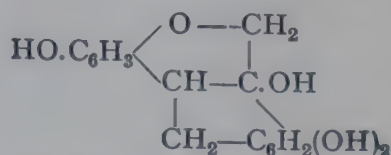
The extract is settled in large tanks, filtered through cloth, and concentrated by evaporation. Up to  $10^\circ$  Bé. the extracts are fluid;  $30^\circ$ - $40^\circ$  Bé. yield solid extracts. Logwood is exclusively used for *black* dyeing of silk, using an iron salt and some yellow colouring matter to kill the blue tone. Also used for dyeing and printing black and grey shades on calico and wool, and for shading with a blue tone other colouring matters. Except for black silk its use is being displaced by artificial colouring matters. For **Dyeing Processes**, see pp. 551, 552.

**Tests.**—Logwood chips may be adulterated with syrup extracts containing tannin (*e.g.*, chestnut extract) or “foots” or with excess of moisture. (1) A microscopic examination usually reveals nature of contamination. (2) Estimate the moisture (drying weighed quantity chips at  $100^\circ$  C.). If it contains more than 14 per cent. (usual quantity) it is adulterated and may take up 40 per cent. moisture. (3) The only reliable test is an actual dyeing test with white wool, made with definite weights of wood, thoroughly extracted, and definite weights of mordants.

### Red Colouring Matters

**Madder** (German, *Krapf*).—Now displaced by artificial alizarin (p. 451), which see.

**Redwood, Brazil Wood** (*Rotholz, Bois rouge*).—Many different varieties are known (*Family* Leguminosæ, genus *Cæsalpinia*, found in East Indies, Central and South America, etc.). It contains the colourless base **brasilin**,  $C_{16}H_{14}O_5$ , which when carefully oxidised furnishes the red colouring matter **brasilein**,  $C_{16}H_{12}O_5$ . The constitution of brasilin is believed to be as shown—



but the substance has not as yet been synthesised. The colour is not very fast, and its use is dyeing cotton, and printing to produce mixed shades; also for wool and oils.

**Santalwood** (*Sandelholz*, East Indies) contains 16 per cent. of **santalin**,  $C_{16}H_{14}O_5$ ; the extract is used for colouring confectionery, liqueurs, tinctures, etc.

**Archil** (*Orseille, Oricello, Orchilla*) is obtained from the algal genera *Rocella*, *Variolaria*, and *Lecanora*, by extracting the plants with water and warming the liquor with ammonia, when the archil is precipitated as a paste. The actual colouring principle is **orcin**,  $C_6H_3(\text{CH}_3)(\text{OH})_2$ , which in the presence of air and ammonia oxidises to the violet dye orcein,  $C_{28}H_{24}N_2O_7$ .

**Litmus** (*Lachmus, Tournesol*) is likewise obtained from certain algæ (species of *Rocella* and *Lecanora*) in the East Indies, tropical America, and Canary



Islands, Scandinavian and Mediterranean coasts. The algæ are dried, ground, mixed with ammonium carbonate, potash, and lime, allowed to stand three weeks, when the material ferments and produces a blue colour. More ammonia and chalk are added, and the mass pressed into cubes and dried. Contains several colouring matters (azolitmin, litmum, etc.), which in free state are red, but with alkali form **blue** salts (hence acids turn litmus red, alkalis blue). Used as an indicator in chemistry, also for colouring liqueurs, confectionery, preserved fruit, etc. etc.

**Carotene** is the yellow-red colouring matter of carrots, and is used for colouring butter and cheese.

**Alkanet**,  $C_{15}H_{14}O_4$ , is obtained by extracting the root of the *Alcanna tinctoria*, and is used for colouring oils, salves, hair-oils, etc., and other cosmetic articles, since it is soluble in such media and fast.

**Carmine (Cochineal)** is a colouring matter contained in the females of the insect *Coccus cacti* (Mexico and Central America). The females are collected shortly before the laying season, killed by steam, dried, and sold as colouring matter under the name **Cochineal**. The colouring matter is **carmine**, which is obtained by extracting the insects with boiling water, precipitating with alum, washing and drying; it is stated to be an **aluminium calcium protein** compound of the carmine colouring matter. The cochineal insects contain 10 per cent. carminic acid,  $C_{22}H_{22}O_{13}$ , which is hydrolysed by dilute sulphuric acid into sugar and **carmine red**,  $C_{11}H_{12}O_7$ . **Carmine** is used for making face powders, colouring sweets, puddings, etc., being non-poisonous (see also p. 552).

**Lac-dye**, a product similar to cochineal in origin and use, is obtained from **gum-lac**, an exudation product formed by certain tree-boring insects, by extracting with sodium carbonate solution. The residue left behind forms the ordinary **shellac** (see pp. 348, 552).

The **Purple** of the ancients was obtained from a snail inhabiting the sea-coasts of the Mediterranean (see p. 420).

### Yellow, Brown, and Green Colouring Matters

**Fustic** (Brazil wood, yellow wood, *Gelbholz*), from *Morus* (Maclura) *tinctoria*, contains **Morin**,  $C_{15}H_{10}O_7$ , and Maclurin,  $C_{13}H_{10}O_6$  (a non-colouring material). **Morin** gives a yellow lake with aluminium salts, used for colouring wool yellow. Not very fast to light (see p. 552).

**Quercitron**, the yellow powdered bark of the oak *Quercus tinctoria* of North America, contains quercitrin,  $C_{21}H_{22}O_{12} + 2H_2O$ , which, on boiling with dilute acids, hydrolyses into isodulcite,  $C_6H_{14}O_6$ , and the yellow dye **Quercitin** or **Flavin**,  $C_{15}H_{10}O_7$ . Both quercitrin and quercitin form yellow lakes with aluminium and tin salts, and are consequently used for wool dyeing and printing, and largely for shading other colours (see p. 552).

**Persian Berries, Yellow Berries** (*Kreuzbeeren*) contain **xanthorhamnin**, a glucoside which dilute mineral acids hydrolyse into **isodulcite** and the yellow dye **ramnetin**,  $C_{16}H_{12}O_7$ ; the latter substance yields, when fused with potash, proto-catechuic acid,  $C_6H_3(OH)_2.CO_0H$ . Yields yellow lakes with chromium, tin, and aluminium salts, fast to soap and chlorine, but only moderately fast to light. An extract is used as painters' colour and for staining paper and leather yellow (see p. 552).

**Annatto** (Orleans, Anatto, *Terra orellana*), obtained from the fleshy covering of the ruccu tree (*Bixa orellana*) of Central America, contains a yellow colouring matter, **bixen**,  $C_{28}H_{34}O_5$ , and the extract is used for colouring butter, cheese,



margarine (see pp. 75, 87, 546), etc. When annatto has been adulterated with mineral bodies, more than 10 per cent. of ash will be found.

**Turmeric** (*Curcuma*, *Gelbwurzel*).—The powdered root of the *Curcuma longa* and *C. rotunda*, contains a yellow colouring matter, **curcumine**, which can be extracted with ether, alcohol, and alkalis. Although not fast to soap or light, the substance is a useful colouring agent for wool, silk, oil, butter, and cheese (see pp. 75, 87, 546).

**Woad** (Luteolin, Wau, *Gelbkraut*), from *Reseda*, *R. luteola*, contains **luteolin**,  $C_{15}H_{10}O_6$ , and dyes silk a fast yellow (with aluminium salts as mordant).

**Indian Yellow, Purree** (*Purree arabica*, Piuri) is prepared at Monghyr (Bengal) from the urine of cows, fed on leaves of the mango tree. The colouring principle is the magnesium and calcium salt of euxanthic acid,  $C_{19}H_{16}O_{11}Mg + 5H_2O$ . Used as a permanent water and oil colour. If adulterated with chrome yellow it gives a black coloration with  $H_2S$ . If yellow aniline lakes be present the solution remains yellow when concentrated  $HCl$  is added (if pure a colourless solution should result, depositing white flakes of euxanthic acid).

**Cutch** (Cachou, Catechu, Japan Earth) is the brown amorphous extract obtained by boiling with water the wood of various kinds of **Acacia** in India and the East Indies. It contains **catechin** and **catechu-tannic acid**; the latter is used for tanning purposes, and being soluble in cold water may be separated from the catechin by washing cutch with cold water; crude **catechin** remains, which, being recrystallised from hot water, is obtained as fine, white, silky needles, M.P.  $217^\circ C$ ., and of formula  $C_{21}H_{20}O_9$ . Cutch is used in cotton dyeing and printing, producing brown, black, grey, and olive shades, very permanent and fast to light, soap, acids, and bleaching powder. Also used for silk and wood stains (see p. 549), and for preserving jute used in the cable industry.

**Dragon's Blood** is a deep or brown-red resin obtained from species of **Calamus** (India, Sumatra, Moluccas) and used for colouring spirit varnishes, toilet articles, etc., a deep red (see p. 348).

**Gamboge** (*Gumigutt*, *Gutti*) is the resin of *Garcinia Morella* (East Indies, Ceylon); forms a yellow water colour, sometimes used for colouring spirit and other varnishes; poisonous; used in pharmacy (see p. 348).

**Saffron, Crocus** (*Safran*), from dried and powdered flowers of saffron plant, *Crocus sativus* (Orient); used for colouring confectionery (see pp. 75, 87, 546).

A green colouring matter is **Chlorophyll**, found in green leaves and stalks of plants, obtained by extracting grass, etc., with alcohol (or with dilute caustic potash and precipitating by mineral acids). Is fugitive in light, but is used for colouring confectionery, liqueurs, and toilet articles.

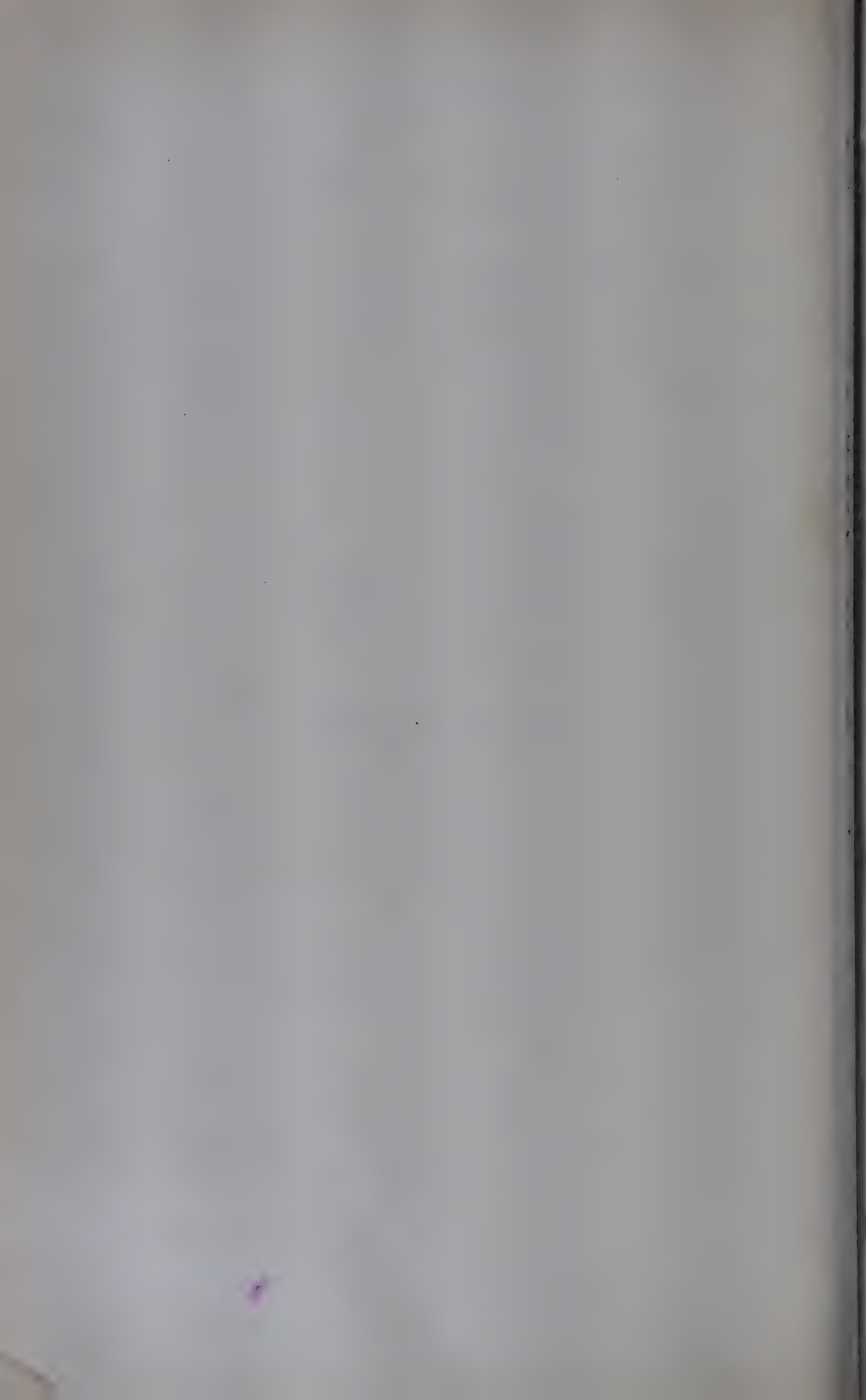
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SECTION XV



The Ink Industry





# THE INK INDUSTRY

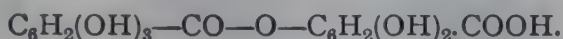
BY G. MARTIN, Ph.D., D.Sc. (with revisions)

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## Black Writing Inks

**Gallotannic Inks.**—The ordinary writing inks consist, principally, of the iron salts of gallotannic and gallic acid substances contained in vegetable tannins. Gallotannic acid occurs in gall tannin and has the formula : \*—



When hydrolysed by hot acids, or by fermentation, it breaks down into **gallic acid**,  $\text{C}_6\text{H}_2(\text{OH})_3.\text{COOH}$ . Gallotannic acid yields blue or black compounds with iron salts. Gallic acid, however, produces no coloration with ferrous salts, but the solution on standing gradually oxidises to the ferric state, becomes black, and deposits an insoluble black precipitate. In consequence of this property the ordinary writing inks of commerce are ferrous (unoxidised) inks with gallic or gallotannic acid, and being usually of a very pale colour, have added to them a provisional colouring matter, such as indigo sulphonc acid, soluble blue, etc. The ink on penetrating into the fibres of the paper oxidises after some days into the black ferric compound, and so is not easily removed by washing. The presence of indigo increases the permanency of the ink, and makes it more resistant to the action of bleaching agents.

A good ink of this nature consists of an extract of 42 parts Aleppo galls in 120 parts of water, mixed with 1·2 parts of indigo solution (indigo sulphonc acid), or some other blue aniline dye, such as aniline blue, fast blue, etc. To this are added 5·5 parts of ferrous sulphate and 2 parts of metallic iron dissolved in crude acetic acid (pyroligneous liquor). A certain amount of anti-septic—say 2 lbs. phenol to 1,000 gals. of ink—is usually added to prevent the ink from becoming mouldy.

*State of Massachusetts official ink* contains: Dry gallotannic acid, 23·4; gallic acid crystals, 7·7; ferrous sulphate, 30; gum arabic, 25; dilute hydrochloric acid, 25; phenol, 1; all dissolved in 1,000 parts of water.

*Dieterich* recommends the following ink: 60 g. tannin are dissolved in 540 c.c. of water; 40 g. of ferric chloride solution, containing 4 g. of iron, are mixed with 1 g. of sulphuric acid and 400 c.c. of water. The solutions are mixed, boiled ten to fifteen minutes, and then 30 g. of sugar and 10 g. of aniline water blue 1B are added. The ink flows easily from the pen with a deep blue colour, and dries blue-black; copies taken are blue at first but become black.

**Gallic Acid Inks.**—When gallotannic acid is hydrolysed by acid or allowed to ferment it breaks up into gallic acid,  $\text{C}_{14}\text{H}_{10}\text{O}_9 + \text{H}_2\text{O} = 2\text{C}_7\text{H}_6\text{O}_5$ . After the conversion of gallotannic acid into gallic acid twice as much ink is produced from a given amount of ferrous sulphate—a fact which has given rise to Gallic Acid Inks, which we will briefly describe :—

**Ink from Fermented Gall Extract.**—200 parts of powdered Chinese galls are kept moist (but not wet) at 20°-25° C. until mouldy (eight to ten days), when most of the gallotannic acid has fermented into gallic acid. The galls are thoroughly extracted with hot water, talc is added, the

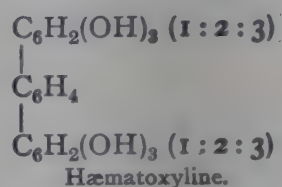
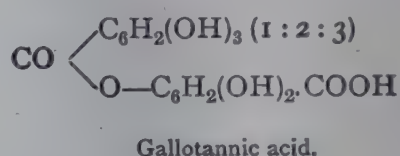
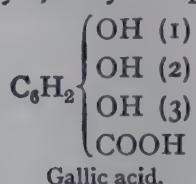
\* Recent research has shown that the tannins consist of several complex substances.



solution filtered, and made up to 1,000 parts by weight; then 100 parts of ferric chloride solution containing 10 per cent. of iron are added, and the ink left for two weeks in closed flasks, decanted, and a provisional colour added, which, for a **blue-black ink**, consists of 3 parts of phenol blue in 400 parts water + 1 part phenol; this is added to 600 parts of the ink solution, the whole kept for a week in a loosely-covered flask, and then decanted. A **black ink** is given by 10.5 parts aniline green + 9 parts ponceau red R + 1 part phenol blue 3F dissolved in water and added to the ink solution.

**Ink from Hydrolysed Tannin Solution.**—100 parts of tannin, 100 of water, 200 of ferric chloride solution (10 per cent. iron), and 10 parts of crude hydrochloric acid (sp. gr. 1.16), are heated for ten hours at 80°-90° C. (in order to hydrolyse the gallotannic acid into gallic acid), then diluted with 700 parts of hot water, heated to 80° C. for one hour, cooled, kept in a closed bottle for two weeks, filtered, and diluted to 1,000 parts. A provisional colour must be added, since the writing at first is barely susceptible, although it ultimately oxidises to deep black. The provisional colour may be the same as that in the preceding ink.

**Chemical Nature of Tannin Inks.**—Schluttig and Neumann showed that benzene derivatives containing three or more hydroxyl derivatives in juxtaposition yield permanent inks with iron compounds. For instance, hydroquinone,  $C_6H_4(OH)_2$ , does not yield an ink with iron salts, whilst gallic acid, gallotannic acid, and hæmatoxyline (the colouring principle of logwood), each of which contain three adjacent hydroxyls, all yield permanent inks with iron salts:—



The precise nature of the iron compounds which occur in tannin inks is unknown; no doubt several individual bodies exist and contribute to the effect. The experiments of Pelouze, Wittstein, and Schiff point to the existence of the basic tannate  $(C_{14}H_9O_9)_3Fe-Fe(C_{14}H_9O_9)_3$ . Chemically, however, the whole subject is very obscure.

**Tannin Materials for Inks.**—Tannins of various kinds occur widely distributed in the vegetable kingdom, and consequently there exist a large number of vegetable products from which inks can be made. Among these may be mentioned: **Galls**, vegetable excrescences formed upon the branches, shoots, and leaves of trees by the puncture of the young tissues by the females of certain insects for the purpose of depositing eggs. Many varieties of galls occur, such as **Oak Apple Galls**, **Aleppo Galls** (Turkey or Levant Galls), **Chinese Galls**, **Japanese Galls**, **Acorn Galls**, etc. These contain from 40-70 per cent. of tannin, estimated as gallotannic acid.

Other ink-making materials are: **Chestnut Extract** (from the wood or bark of chestnut tree), **Sumach Divi-Divi**, **Myrobalans**, **Valonia**, **Oak Bark**, etc., all of which materials are rich enough in tannins to yield good inks. (See also under **Leather Manufacture**, p. 573).

Tannins may be divided into "iron-blueing" and "iron-greening" according to the colour of the precipitate they form with iron salts. Only the iron-blueing tannins are suitable for the manufacture of black ink. Oak-bark tannin, although an iron-greening tannin, contains a substance giving a blue precipitate with iron salts and consequently can be used for ink manufacture. Tannins suitable for leather (see **Leather Manufacture**), are often unsuitable for inks.

**Statistics.**—The amount of galls imported into Britain was 18,500 cwt. (value, £62,000) in 1906, and 15,600 cwt. (value, £37,000) in 1910. The amount of the other vegetable tannins is given under **Leather**.

**Logwood Inks.**—Logwood extract (see **Logwood**, **Natural Colouring Matters**) is often added to iron gall inks, improving its colour without injuring its permanency. A common recipe is 3 parts of galls, 1 of ferrous sulphate, 1 of logwood, in 50 parts of water, with gum arabic in proportion of 1 part to 40 of ink.

A copper logwood ink consists of logwood extract, 20 kilos. in 200 kilo. water, mixed with 10 kilos. of ammonium alum previously dissolved in 20 kilos. of boiling water, 0.2 kilo. sulphuric acid, 1.5 kilos. copper sulphate in 20 l. of water. A provisional colouring matter (indigo sulphonie acid, phenol blue, etc.) must be added. The copper destroys steel pens.



**Dieterich's School Ink** is a bichromate logwood ink, consisting of 200 parts of a 20 per cent. logwood extract solution diluted to 500 c.c. and heated to 96° C. Then a solution of 2 parts of potassium bichromate, 50 of chrome alum, and 10 of oxalic acid dissolved in 150 of water are added drop by drop, the mixture maintained at 90° for thirty minutes, and then diluted to 1,000 parts, 1 part of phenol added, and the whole allowed to stand two to three days, decanted, and is then ready for use.

**Black Aniline Inks.**—A black ink stylographic pen consists of a solution in water (1 part dye to 80 parts water) of the various brands of water-soluble nigrosines (the sodium salts of the sulphonated nigrosines, see **Dyes**, p. 475). Such solutions have no action on metallic pens, and dry well, but lack the permanency of a good iron gall ink. Induline blue (B) (p. 475) forms a similarly constituted blue ink.

### Coloured Writing Inks

These are usually made from water-soluble aniline dyes such as the following, the proportions being 1 part dye to 50-80 parts of water.

**For Red Inks.**—Eosin, erythrosin, ponceau scarlet, or cotton scarlet.

**For Green Inks.**—Neptune green S.G., diamond green G.

**For Blue Inks.**—Indigo carmine, or soluble blue T.

A good blue ink (fast) is made by triturating 10 parts freshly precipitated Prussian blue, 1 part of oxalic acid, and adding water gradually.

**Violet.**—Acid violet 4B.L.

**Yellow.**—Fast yellow or tartrazin in water.

**Gold Ink.**—Gold leaf, mixed with honey, is ground fine, washed, dried, and suspended in gum-arabic (1) + 1 of soluble potash glass dissolved in 4 of water. Substitutes for gold are Dutch leaf or bronze powder. **Silver ink** = powdered silver (or Aluminium foil) rubbed up with gum or the preceding medium.

**Essentials of a Good Writing Ink.**—(1) The writing should be permanent (2) The ink should flow readily from the pen. (3) It must penetrate deeply into the fibres of the paper without passing right through. (4) It must not become mouldy or thick in the ink pots. (5) It must not extensively corrode metallic pens. (6) The writing must rapidly dry and should not be sticky—unless it is a copying ink.

### Copying and Hectographic Inks

**1. Writing Inks.**—Ordinary iron-gall and logwood writing inks are rendered capable of giving one or two good copies in a press, or less readily in a rapid-roller copying machine, by the addition of glycerol, gum, sugar, glucose, etc., to a previously concentrated ink.

Better results are obtained by using concentrated solutions of the water-soluble aniline dyes with the addition of a small proportion of glycerol.

Many of the copying inks on the market contain an excess of acids and gums or other thickening substances which are not only unnecessary but actually deleterious.

Any of the basic dyes are suitable for the manufacture of copying inks, the proportion to be used varying with the strength of the dye and the number of copies required; e.g., **Violet Inks**—Methyl Violet 3B; Crystal Violet [B]; Methyl Violet O and III. extra N. **Red Inks**—Eosin, Diamond Magenta; Magenta Powder; Safranin T extra [B]. **Black Copying Ink**—Diamond Green B and G [B] + Diamond Magenta + Chrysoidine. Also aniline black dissolved in alcohol and glycerol.

**Hectograph inks** are merely concentrated copying inks. Occasionally it is desirable to add a small proportion of alcohol and a very slight excess of a weak acid to prevent thickening due to deposition of the dye.

**Typewriter Ribbon Inks.**—The manufacture of typewriter ribbons has increased enormously in recent years. There are quite a number of firms who have placed on the market machines for cutting, inking and winding typewriter ribbons; whilst the manufacture and cutting into the required widths of the fabric is a separate branch of the industry.

The firms selling inking machines also provide suitable grinding mills and formulæ for manufacturing the inks.

Typewriter ribbons may be divided into two classes:—

(a) **Record or Non-Copying.**—The only really permanent ribbons are those inked with a composition having lamp or a similar carbon black as a basis.

For use on a modern inking machine the lampblack, or in the case of coloured ribbons an aniline lake, is ground in a suitable mill with a non-drying oil, thickened if necessary with petroleum jelly. Occasionally a little volatile solvent such as petrol, carbon tetrachloride, etc., is used to facilitate absorption.



Oil-soluble aniline colours may also be employed for the manufacture of one-colour record ribbons.

(b) **Copying Ribbons.**—Copying ribbons are made in several varieties.

Slow-copying, two-sided ribbons, for use with the old-fashioned screw press using damp rags; and one or two sided-rapid copying ribbons for use on machines such as the Roneo Copier using rolls of prepared paper.

The slow-copying ribbons contain a lake or colour and a small proportion of a water-soluble dye, whilst the rapid roller ribbons consist of a strong water-soluble dye ground in a non-drying oil. It is not necessary to add glycerol or indeed any other substance beyond the oil and dye.

**Testing Typewriter Ribbons.**—A well-made typewriter ribbon should give fine sharp impressions, exhibit no tendency to fill the type and be cleanly in use and last a reasonable time without losing its writing or copying properties or wearing into holes.

The general character of a ribbon can best be judged by an extended and careful test carried out on the machine for which the ribbon is intended.

For purposes of comparison short definite lengths of the ribbons to be tested should be worked backwards and forwards through the typewriter a stated number of times and the results compared.

If the letter "e" is alone used for this test the type-filling property can also be judged.

To test the life of a ribbon a special testing machine similar to that described in the United States Bureau of Chemistry Bulletin No. 109 revised, p. 51, is necessary.

Some idea of the life of a ribbon can be obtained, however, from the results obtained in the character and filling tests described above.

In order to obtain concordant and comparable results, it is absolutely necessary that the tests should be carried out under exactly similar conditions.

A good copying ribbon should give eight to twelve readable copies from one original. The copying test should preferably be carried out on a "Copier" in order to obtain comparative results.

As a rule one-sided ribbons give neater work and are cleaner to handle than two-sided ribbons and are absolutely non-filling, but the life is somewhat shorter than that of a two-sided ribbon. One-colour record ribbons are always two-sided.

Record ribbons may be tested for resistance to sunlight and chemical reagents if necessary.

As mentioned previously only black record ribbons are absolutely permanent, but for ordinary commercial use a good copying ribbon is generally preferred owing to the convenience of being able to obtain actual copies of the correspondence without using carbon paper.

Unless actually exposed to sunlight or to the action of chemicals both the original and copies are sufficiently permanent for commercial office use.—FRANK B. GATEHOUSE, F.C.S.

**Copying Ink Pencils** are made by making a paste of powdered graphite and kaolin clay with a very concentrated solution of methyl violet, pressing into sticks and drying.

**Manifold Copying Apparatus.**—The block of *Rosefeld's* apparatus (English Patent No. 2,256, 1879) consists of gelatine, glycerol, molasses or sugar, acetic acid, iron oxide, and sodium bisulphite. The ink is aqueous methyl violet.

The drawback of gelatine beds is that they become ultimately saturated with ink. *Smith's* apparatus (English Patent No. 7,149, 1888) obviates this, as ink is sponged or scraped off when used. The slab consists of china clay, starch, glycerol, and water. The ink is an aniline dye in water, alcohol, and hydrochloric acid. Similar pads consist of water (10), dextrine ( $1\frac{1}{2}$ ), sugar (2), gelatine (15), glycerol (15), zinc oxide (2). Barium sulphate is sometimes used instead of zinc oxide, while the addition of soap makes the surface smooth and easily washable.

### Marking Inks

(a) **Natural Vegetable Inks.**—A number of plants give black marking inks. Among these we may mention the juice of *Coriaria thymifolia*, a plant occurring in New Granada and New Zealand ("ink plant").

The fruit of the Indian tree, *Anacardium orientale* or *Semecarpus anacardium*—the "marking nut"—yields a juice which when mixed with lime water or alkali marks linen an almost indelible black. Similar inks are prepared from the **Cashew Nut** (fruit of *Anacardiaceæ*, *A. occidentalis*, found in India, West Indies, tropical South America), the *Rhus toxicodendron* (North America), *Rhus venenata* (North America), and *Rhus radicans*.

(b) **Chemical Marking Inks—Silver Inks.**—These inks contain a silver salt—usually silver nitrate—the reduction of which within the fibres of the material leaves an insoluble black deposit.



Thus *Dieterich's* marking ink consists of ammoniacal **silver nitrate** solution with the addition of gum arabic and a provisional colouring matter such as carbon black or a soluble dye. The ink penetrates the cloth fibres and decomposes to form metallic silver; this decomposition is accelerated by hot ironing. The final marking is very permanent and can only be removed by potassium cyanide solution.

**Aniline Black Marking Inks** can be prepared by mixing aniline black with acidified alcohol and shellac solution. They are not very permanent and readily removed by alkalis. Better aniline black inks are those in which the pigment is produced inside the fibre. For example:—

Part A. Copper chloride 8.52 grams, sodium chlorate 10.65 grams, and ammonium chloride 3.35 grams, dissolved in 60 ml. of water.

Part B. Aniline hydrochloride 20 grams, gum arabic 7 grams, glycerine 1 gram, dissolved in 45 ml. of water.

Mix four parts of "B" with one of "A" before use. The green writing darkens on exposure to air and eventually becomes black, the change is more rapid with heating. Single solution marking inks of the same type are on sale, but these require accurate formulation or decomposition will occur in the bottle. The most important controlling factors are the pH of the final solution, and the acid used in the aniline salt, thus aniline acetate is more readily decomposed.

### Miscellaneous Inks

**Waterproof and Indian Inks.**—Liquid Indian inks consist of pigment dispersions in gum solutions, usually carbon black in gum arabic solution. If the binder is insoluble in water, waterproof inks are obtained, these usually contain shellac dissolved in alcohol or dilute ammonia, or one of the spirit soluble synthetic resins. The pigments ground in to these media can be any of those suitable for printing inks.

### Chemical Inks for Writing on Metals

**Black Ink for Iron, Zinc or Brass.**—An ink of the following composition gives dull black writing: copper sulphate 5, 5 per cent. acetic acid 1, gum arabic 2, carbon black 1, and water 5.

**Black Ink for Copper or Tin.**—The recipe is as that for iron, etc., but with the acetic acid replaced by ammonium chloride 3, and hydrochloric acid 3.

**Black Ink for Silver.**—A 7 per cent. solution of the double chloride of sodium and gold gives brown writing turned black by the action of light.

**Foertsch's Pencil for Glass** is made by stirring Prussian blue into a melted mixture of 8 parts white wax and 2 parts tallow, and when nearly cold rolling into a pencil on a slab and covering with a paper case.

### Control and Analysis of Writing Inks

**Control.—Acidity.**—Gallotannic inks require the addition of strong acids to prevent the precipitation of oxidised products in the bottle. The acids usually added are hydrochloric, sulphuric, or oxalic. The amounts of these added acids and the final acidity must be as low as is consistent with stability, since excess acid leads to corrosion of steel pens and possibly destruction of the dyestuff present. Gallic acid inks do not require added acids as they are more stable, but they have disadvantages in slow paper penetration and a low iron content, since gallic acid is not readily water soluble.

**Estimation of Acids in Inks.**—The corrosive acids can be estimated by comparative tests on the rate of increase in weight of an immersed steel nib, or by electrometric titration. The total corrosive and weak organic acids are



estimated by bleaching with hydrogen peroxide solution and titrating the acid with alkali solution and phenol phthalein. A blank must be performed on the peroxide solution. The alkalinity of new glass bottles may cause instability in acid stabilised inks unless precautions are taken. The approximate acidities of commercial gallotannic inks in terms of ml. of N. alkali neutralised by 10 ml. of ink are as follows: strong acids 1.3–2.5; weak organic acids 1.3–3.0.

**Solids and Iron Content.**—Three quantities should be determined, the total solids by evaporation of the water at a low temperature, total ash by ignition, and the iron content by dissolving the ash in hydrochloric acid and estimating volumetrically. Typical values for commercial inks are: total solids 3.6 per cent., total ash 0.8 per cent., iron content 0.3 per cent.

**Control of other Properties.**—The viscosity of inks should not vary a great deal, and is generally about 1.25 times that of water. Shade should be checked in all inks containing dyestuffs.

**Analysis.**—The composition of an ink can be found by obtaining the solids, ash, and iron content, and then applying specific tests for the detection of the components.

**Gums and Dextrin.**—These are obtained by precipitating from the ink with twice the volume of rectified alcohol, filtering and drying. Dextrin is strongly dextro-rotatory when dissolved in water, while gum gives a rose-violet colour with phloroglucinol after boiling with concentrated hydrochloric acid.

Glycerine is obtained by alcoholic extraction of the total solids and is readily identified by normal chemical tests.

Preservative such as phenol or salicylic acid is likewise obtained by ethereal extraction of the solids.

Dyestuffs can be fully analysed by chemical tests, but can usually be sufficiently classified by examination of their dyeing properties towards wool and cotton from portions of the ink which are weakly acidified, strongly acidified, and made alkaline respectively. Indigo carmine, for instance, is fixed on wool in an acid bath, and redissolved in an alkaline bath.

### Standards for Writing Inks

(H.M. Stationery Office, 1934)

**General Service Blue-black.**—The ink shall be a gallo-tannate ink containing not less than 0.25 per cent. of iron in a suitable ratio with the tannin substances present.

The acidity of the ink shall be the minimum consistent with good performance.

The ink must produce a good blue-black colour after being blotted and a deep black colour after fourteen days. The ink must remain clear and without sediment, and must retain its writing properties when evaporated to one quarter of its original volume.

### Printing Inks

With very few exceptions printing inks consist of intimate dispersions of pigments in non-aqueous media. The type of medium and its relative proportions with the pigments depend principally on the printing method and the manner in which the ink is required to dry. The drying of an ink needs the greatest attention, and most printing ink research is devoted to producing faster drying without impairing the other printing properties. The principal methods of drying are as follows:—

**Absorption.**—Although in most printing processes some absorption takes place, it is in newspaper printing that this is the sole method of drying. The requirements for absorption drying are a rough surfaced absorbent paper and a thin vehicle.



**Oxidation.**—The method relies on the reaction between drying oils, such as linseed, and atmospheric oxygen to form a hard oxidised “skin.” This oxidation is greatly accelerated by some metallic salts, notably the oil soluble oleates and naphthenates of cobalt, lead, and manganese.

**Evaporation.**—This can take place in an ink by the normal evaporation of a volatile solvent or by use of a solvent which will only evaporate appreciably when the printed ink is heated. The resin dissolved in the solvent remains as a binder for the pigment film.

### Raw Materials for Printing Inks

**Pigments.**—The number of available pigments has increased greatly in recent years owing to the introduction of many new organic colours. These colours are very strong in many cases, so that most coloured inks contain “extender” pigments, these have practically no colour when ground in oils and do not impair transparency. They serve the functions of producing an ink of the required strength, improving the printing properties of the poorer working pigments, and cheapening the cost. The commonly used pigments and dyes are as follows:—

**Colourless extenders.**—Alumina hydrate, blanc fixe, precipitated chalk, and china clay.

**Whites.**—Titanium dioxide, zinc oxide, antimony oxide, and lithopone.

**Yellows.**—Lead chromate yellows, “Hansa” yellows, benzedine quinoline, and tartrazine yellows.

**Blues.**—Prussian blue, ultramarine, phthalocyanine blues, “Reflex” blues, and “Fanal” blues (triphenylmethane dyes laked with phosphomolybdic acid).

**Browns.**—Iron earth pigments.

**Reds.**—Orange chrome, red lake pigments, orthonitraniline orange, and alkali “Lithols.”

**Greens.**—Phthalocyanine green, “Fanal” greens, and mixtures of chrome yellows with blues.

**Black.**—Practically all black inks are made with carbon black prepared from natural gas. Other blacks are bone blacks, and vegetable blacks which also consist of finely divided carbon.

**Drying Oils.**—Linseed oil is largely used in printing inks, usually in one of the polymerised grades which can be obtained in viscosities varying between 1 and 120 poises.

Castor oil is a non-drying oil, but can be thermally dehydrated to form a drying oil with conjugated double bonds. This oil can then be polymerised to any viscosity between 5 and 120 poises.

Tung oil is the fastest drying oil and is very readily polymerised at temperatures much lower than those used for linseed and castor oils.

**Resins.**—All spirit or oil soluble resins are in use, the commonly used types being as follows:—

Drying oil modified alkyds, produced by condensing and polymerising together phthalic anhydride, glycerol and drying oil.

Rosin modified oil soluble cresol and phenol-formaldehyde resins.

Spirit and oil soluble 100 per cent. substituted-phenol-formaldehyde resins.

Lime and zinc hardened rosins, ester gum, and rosin adducts such as maleic anhydride-rosin condensates.

Natural resins such as copal, manila copal, kauri, shellac and dammar.



### Letterpress Inks

Inks for printing from a raised surface fall into two main categories, newspaper inks and general book and illustration inks.

**Newspaper Inks** dry by absorption and so the medium is thin, having a viscosity of about 5 poises, and is practically always a mineral oil blend. Typical recipes are:—

1. Carbon black 15, prussian blue 10, mineral oils 75.
2. Carbon black 20, oil soluble blue dyestuff 1, mineral oils 79.

The addition of blue is necessary to counteract the brown tone of carbon black; it can be added as pigment or as dyestuff. Dyes tend to stain the printing rollers and may cause "strike through," but they enable a stronger ink to be produced. Newspaper inks may also contain cheap non-drying oils such as rosin oil and resins, to improve the printing properties. Bitumen is also used. Grinding is usually carried out by means of a single-roll or ball mill, the final product varying in consistency from that of paint for fast-running rotary machines to that of a normal letterpress ink for flat-bed news machines.

**General Book Inks.**—First in importance are the "jobbing" blacks for general type printing, the art tricolour and black inks for illustration work. The former type of ink is fundamentally an oxidation ink based usually on polymerised linseed oil; it is varied according to the particular paper to be printed on, thus:—

1. Carbon black 25, prussian blue 5, "Reflex" blue 1, mixed Co., Pb., Mn., Oleate driers 3, polymerised linseed oil (40 poises) 78. This is an ink suitable for printing on papers such as imitation art, bank, bond, "cotine," etc.
2. For printing on a support such as a metal foil or on a cellulose film a harder drying ink is needed, and the 40-poise linseed oil would be replaced by a resin varnish such as: Rosin modified phenol-formaldehyde resin 20, polymerised linseed oil (20 poises) 80.

**Art Paper Inks** are the best quality inks produced, they can be straight oxidation inks similar to the jobbing black, but are more likely to be one of the modern type quick-setting inks. These dry by a combination of absorption and oxidation, the initial absorption of part of the vehicle producing a rub free print within a few minutes of printing; this oxidises to a hard film overnight. The tricolour inks are used in producing high quality coloured prints, the shades of the three inks being accurately matched to correspond with the colour filters used in preparing the printing blocks. The colours usually used are as follows:—

**Opaque Yellow.**—This is printed first and contains about 65 per cent. of a mixture of lead chromates, the remainder being the varnish plus driers, etc.

**Transparent Red.**—This is printed second or third and contains a mixture of fast red organic pigments totalling about 20 per cent., and about 20 per cent. of extender pigments, usually alumina and blanc fixe.

**Transparent Blue.**—This is usually based on the very stable phthalocyanine blue 10 per cent., and a further 30 per cent. of extender pigments.

A transparent yellow can be used in which the opaque lead chromate is replaced by organic yellows; this ink is often printed after the red and the blue. Printing inks of letterpress and litho consistency are mixed in dough-type mixers and ground on steel three-roll mills.

### Lithographic Inks

These are similar to letterpress inks, but the method of printing demands certain additional properties. First among these is that the ink must possess



good water resistance, otherwise the water used in damping the lithographic printing plate will mix with it, causing the ink to lose its transference properties. Secondly, the ink must be stiffer and stronger than a letterpress ink as the printing film thickness is not very great and is limited by the process. The ink therefore contains a greater percentage of pigments than a letterpress ink.

### Gravure Inks

These resemble thin paints, and they consist of pigments dispersed in a resin spirit solution. As the ink dries by evaporation of the solvent, drying is very rapid and is often accelerated by passing the printed reel of paper over steam-heated rollers. Points peculiar to gravure inks are that the pigment should be very well dispersed by grinding the ink through a single roll or ball mill in order to prevent settling, and the pigment should contain no gritty particles as these will scratch the printing plate, causing the thin continuous lines sometimes seen across gravure prints.

The solvent used in gravure inks is usually a compromise between all the desirable properties required. These properties include strong solvent action for resins, the right degree of volatility, non-inflammability, non-toxicity, and cheapness. The solvents generally used are xylol, petrol, and sometimes alcohol. Alcoholic gravure inks are usually used for printing food wrappers, where the slight after-smell of xylol is objectionable.

The resins used can be any hard natural or synthetic resins which are soluble in the solvents used, for instance, lime and zinc hardened rosins, rosin modified cresylics, polyvinyl and polystyrene resins, copal ester gum, and bitumens (blacks only). For alcoholic gravure inks, shellac, 100 per cent. phenolic resins or polyvinyl resins are used.

The pigments used are the same as those for letterpress inks with the omission of hard pigments such as iron oxides. The ratios of pigment to resin and solvent depend on whether a glossy or a matt ink is required; a pigment resin ratio of about 1 to 1 giving a glossy ink, and one of 2 or 3 to 1 giving a matt ink, varying, of course, with the nature of the pigment and the resin.

### Miscellaneous Inks

**Gold and Silver Inks** are superseding the old method of dusting bronze or aluminium powders on to a sticky printed varnish. The medium for these inks must have a very low acid value to prevent interaction with the metallic particles, and often contains wax to assist in the flotation of the metal particles which give the metallic lustre to the print. Gold inks must be mixed as required since they do not keep.

**Aniline Inks** are printed by a letterpress process, often using rubber blocks. The ink is a thin alcoholic solution of a dyestuff with a laking agent, usually tannic acid; it dries very quickly and is suitable for printing coarse designs on paper bags, etc.

**Overprinting Gloss Inks** are highly polymerised varnishes containing wax, which are printed over illustrations in order to impart a very high glossy finish.

### Modern Developments

**Heat Setting Inks** contain vehicles consisting of a synthetic resin and a solvent which is not appreciably volatile at room temperature, but which is evaporated from the ink by the application of heat to the surface of the paper after it is printed. All types of paper can be printed and, as the ink is dry almost instantaneously, the paper can be cut and folded on the same machine as in newspaper printing, but with a much superior printed result.

**Steam Setting Inks** contain a vehicle which is sensitive to water, for example, a synthetic resin dissolved in a polyalcohol. A steam jet after printing precipitates the resin from solution, the diluted alcohol quickly soaks into the paper and a dry pigment resin film is left. A recipe based on a patented varnish might be: Lead chromate 50, bronze blue 10, varnish 40. The varnish, consisting of maleic anhydride-rosin ester dissolved in diethylene glycol, to give a viscosity of about 20 poises,

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## SECTION XVI

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### The Paint and Pigment Industry





# THE PAINT AND PIGMENT INDUSTRY

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## LITERATURE

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## PIGMENTS

THE Chemistry of Pigments is a study of supreme importance—a fact which painters and manufacturers have only recently begun to appreciate. In the present section the limitation of space prevents our doing anything like full justice to the subject, but an attempt is made to lay before the reader the main outlines in question; for further detail reference should be made to the works cited above.

Pigments may be classified according to several different schemes. Thus, for example, the painter groups his pigments from the point of view of colour. The chemist, on the other hand, considers their chemical composition. Here, again, two methods are possible. We may group the pigments according to the chemical nature of their bases, or of their acid content. Neither system is perfect, but we shall adopt the former in these pages.

### Pigments Containing Lead

**White Lead.**—One of the oldest and most important pigments belonging to this group is white lead or lead carbonate. It was known to the Romans and Greeks at the beginning of the Christian era, the pigment being obtained from the mineral cerussite, in which form lead carbonate occurs in nature. The modern painter, however, employs the artificial product only. Although numerous methods have been invented and patented for the manufacture of white lead, the best results are apparently yielded by the old *Dutch Process*, which we will therefore describe first.

Several thousand earthenware pots are about one-third filled with a 2-3 per cent. solution of acetic acid, and are built up into stacks inside large sheds specially built for the purpose. The method of working is as follows: The floor of the shed is spread with spent tan, and upon this a layer of crucibles is set, and covered with perforated sheets of lead, known as “blue lead.” Wooden boards are now laid on the top, and these in turn are covered with tan, carrying another layer of pots, and



so on, until the numerous layers have completely filled the sheds. The whole is now left alone for a period varying from three to four months, according to circumstances. During this time the tan ferments, and the heat thus liberated serves to vaporise the acetic acid in the pots. The leaden sheets are thereby converted by degrees into lead acetate, which in turn is decomposed by the water vapour and carbon dioxide (evolved from the decaying tan) yielding lead carbonate. On opening the stack the sheets are scraped, and after washing and crushing (which flattens out any unchanged blue lead, and renders it easy to separate) the pigment is ready for the market.

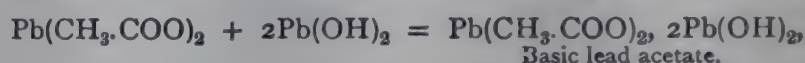
According to Liebig the following successive changes take place :—

1. 
$$\text{Pb} + 2\text{CH}_3\text{COOH} = \text{Pb}(\text{CH}_3\text{COO})_2 + \text{H}_2.$$
2. 
$$2\text{Pb}(\text{CH}_3\text{COO})_2 + 2\text{H}_2\text{O} = \text{Pb}(\text{CH}_3\text{COO})_2 \cdot \text{Pb}(\text{OH})_2 + 2\text{CH}_3\text{COOH}.$$
  
Basic lead acetate.
3. 
$$3\text{Pb}(\text{CH}_3\text{COO})_2 \cdot \text{Pb}(\text{OH})_2 + 4\text{CO}_2 = 2(2\text{PbCO}_3, \text{Pb}(\text{OH})_2) + 6\text{CH}_3\text{COOH}.$$
  
Basic lead acetate.                      White lead.                      Acetic acid.

The acetic acid liberated then attacks more lead, thus repeating the cycle of operations. According to more recent views no hydrogen is evolved (see 1), the acetic acid merely serving to dissolve lead hydroxide formed by the action of air and moisture on metallic lead, thus :—

1. 
$$\text{Pb} + \text{H}_2\text{O} + \text{O} = \text{Pb}(\text{OH})_2.$$
2. 
$$\text{Pb}(\text{OH})_2 + 2\text{CH}_3\text{COOH} = \text{Pb}(\text{CH}_3\text{COO})_2 + 2\text{H}_2\text{O}.$$

The lead acetate then combines with the lead hydroxide, forming basic lead acetate :—



which is then decomposed by the  $\text{CO}_2$ , producing white lead according to the equation (3) above.

The following processes for the manufacture of white lead are important :—

*The German or Chamber Process*, said to be rapidly displacing the other processes, is carried out by suspending 6-20 tons of pure lead in the form of sheets or grids from the roof of a series of chambers provided with flues whereby the admission of air can be regulated. Vinegar vapour, evolved from pans which are placed below the chamber and in which dilute vinegar is heated, is led into the chamber, together with a carefully regulated supply of aqueous vapour, air, and carbon dioxide—the latter being produced by burning charcoal or coke in stoves—and the temperature of the chambers is maintained at  $60^\circ$ - $80^\circ$  C. for eight to ten weeks, when the lead plates are converted into white lead. The quality of the product is good, and stated to be equal to the best white lead prepared by the old Dutch method.

*In the Clichy or French Process*, lead monoxide (litharge) is dissolved in vinegar to form basic acetate (1 molecule of acid dissolving 3 molecules of  $\text{PbO}$ ), then  $\text{CO}_2$  is passed through the clear solution for about twelve hours; most of the lead is precipitated as carbonate, but part remains dissolved as neutral lead acetate. The precipitate of "white lead" is filtered off, more  $\text{PbO}$  is dissolved in the clear filtrate,  $\text{CO}_2$  again led in to precipitate it, and so on. The great advantage of this method is its quickness. The product, however, is variable in quality and inferior to that of either of the processes mentioned above.

*Brown's Electrolytic Process*.—A solution of sodium nitrate containing about 1 lb. of the salt to the gallon is placed in a series of wooden cells, each of which is provided with a porous partition. A strong electric current is passed through the solution, a pig lead forming the anode in each cell, and a sheet of copper the cathode. Nitric acid is liberated at the anode, and attacking the lead forms lead nitrate, which passes into solution. Sodium hydroxide is formed at the cathode: it has no effect on the copper plate. The two solutions are drawn off separately and mixed in quantitative proportions, when they react to form lead hydroxide and sodium nitrate thus :—



The sodium nitrate is used again as a source of nitric acid and sodium hydroxide,



and the lead hydroxide is treated with a solution of sodium bicarbonate with the formation of white lead and sodium hydroxide, thus :—



The white lead is separated from the sodium hydroxide and carbon dioxide passed through the latter, thus converting it into sodium bicarbonate for further use.

This is an extremely rapid method of making white lead. The product is highly amorphous in character, and is said to be equal to the best white lead produced by the Dutch method.

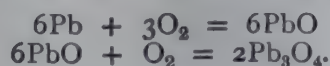
**Properties of White Lead.**—White lead mixes extremely well with oil, and possesses unusually good body, spreading power, and durability. There are, however, two serious drawbacks to its use, namely, the tendency to blacken in the presence of sulphur compounds, and its extremely poisonous nature. When worked in oil white lead loses, in the course of a few months, a little of its opacity, a peculiarity which is probably due to the oil combining with the pigment to form a translucent lead soap.

White lead varies somewhat in composition and character. It should, however, have the composition  $2\text{PbCO}_3, \text{Pb}(\text{OH})_2$ —that of the best white lead produced by the Dutch method—and any departure from this leads to a loss of body if the  $\text{Pb}(\text{OH})_2$  be in excess, and to inability to form a proper emulsion with linseed oil if the  $\text{PbCO}_3$  be in excess.

The cheaper grades of white lead are adulterated, often to a very large extent, and sometimes contain no lead carbonate at all. The most usual adulterant is barytes—barium sulphate—others commonly used are lead sulphate, china clay, and whiting—impure calcium carbonate—and sometimes strontium or barium carbonate, magnesite—magnesium carbonate—and zinc oxide, etc., may be found.

**Red Lead** rivals even white lead in age and importance. It is found in nature as the mineral minium, but, as in the case of white lead, the modern painter uses the manufactured article only.

This is prepared by heating metallic or “blue” lead in a current of air, whereby lead monoxide is formed. This is removed and ground, any particles of unoxidised metal being thereby flattened out, and thus easily removed by means of sieves. On further heating in excess of air for forty-eight hours the monoxide combines with more oxygen and yields triplumbic tetroxide ( $\text{Pb}_3\text{O}_4$ ), commonly known as red lead. These changes may be represented by the following equations :—



In practice 100 lbs. of blue lead yield about 108 lbs. of red lead.

**Properties of Red Lead.**—Red lead mixes readily with the drying oils and rapidly sets, and on this account is largely used by plumbers for packing and luting pipes, etc. Although very permanent and inert in all ordinary circumstances it is subject to the same defect as white lead, namely, that it blackens in the presence of sulphur or sulphur-containing bodies. It cannot, therefore, be safely mixed with such pigments as lithopone and ultramarine. Occasionally it is adulterated with venetian red ( $\text{Fe}_2\text{O}_3$ ), the presence of which is easily detected in the following manner :—

The pigment is subjected to prolonged warming with concentrated nitric acid. If any insoluble residue remains, the presence of silica or sand is to be suspected. If the solution is yellow, the presence of iron may be inferred. Addition of excess of dilute sulphuric acid will cause the precipitation of white lead sulphate, the iron still remaining in solution. On filtering and adding to the filtrate a few drops of potassium ferrocyanide the presence of iron is betrayed by the immediate production of a deep blue colour—Prussian blue.



**Lead sulphate** forms the basis of a large number of pigments known variously as **non-poisonous white lead**, **patent white lead**, **sublimed white lead**, and the like. Although lead sulphate occurs in nature as the minerals **anglesite** and **lanarkite**, these latter are seldom used for the production of the pigment. Manufacturers prepare it by the addition of dilute sulphuric acid to the strong aqueous solution of lead acetate obtained by treating granulated lead with acetic acid. Thus :—



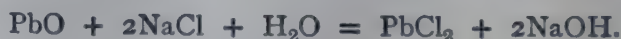
The acetic acid thus liberated is used over again in the production of fresh lead acetate. The precipitated sulphate is allowed to settle, after which it is washed and dried.

Although less poisonous than lead carbonate, lead sulphate has never been as great a favourite amongst painters because its body and spreading power are inferior. It is less sensitive to the action of sulphur than white lead, but it is not advisable to mix it with such pigments as ultramarine and lithopone for obvious reasons.

A basic lead sulphate is being manufactured at Greenford under the name of **Purex** direct from galena or lead sulphide, by combustion in a current of air, whereby oxidation takes place. The resulting compound varies in composition between the limits  $2\text{PbSO}_4.\text{PbO}$ , and  $3\text{PbSO}_4.\text{PbO}$ . It is claimed to be practically non-poisonous (see *The Decorator*, 1911, 9, 251).

Owing to the particular method of preparation—namely, production in the vapour state, and subsequent deposition as a solid without the intermediate formation of a liquid—the pigmentary particles are unusually fine, and thus admit of thorough admixture with oil in preparing paints. This results in the production of paint of exceptional spreading power, but somewhat lacking in body or opacity. In many cases this is not a matter of importance, but for those cases in which opacity is essential the manufacturers recommend a special brand of their Purex in which this objection has been overcome.

**Turner's yellow** is an oxychloride of lead, and appears in the market under many names, such as **Patent yellow**, **Cassel yellow**, **Verona yellow**, **Montpelier yellow**, **Mineral yellow**, etc. It is usually prepared by mixing litharge to a thin paste with a solution of common salt, when the following reaction takes place :—



In about twenty-four hours' time the reaction is fairly complete, the mixture becoming white in consequence of the lead chloride. It is dried, transferred to a crucible and heated to melting until the desired hue has developed.

Turner's yellow possesses good body and mixes well with the drying oils. Of late years, however, it has decreased in popularity in consequence of the extensive rise of the chromes.

**Chrome yellow** or lead chromate is prepared by the addition of potassium bichromate to solutions of lead acetate (see p. 559). Thus :—



Slight variations in the method of manufacture cause marked differences in the hue of the resulting product. Warming with an alkali converts it into the basic chromate, which is orange or red according to circumstances. It is then known as **Orange chrome**, **Chrome red**, **Derby red**, **Chinese red**, etc. All of these pigments, however, are subject to the general fault of lead compounds, in that they are rapidly discoloured in the presence of sulphur or of sulphur compounds.

### Pigments Containing Iron and Cobalt

Some of our commonest and most permanent and useful pigments are compounds of iron.



**Ochre, Sienna, Umber.**—These pigments consist of the hydrated oxide of iron, in the case of sienna and umber a little manganese being present in addition, which probably explains their darker colour. Umber was first found near the ancient Italian town of *Ombria*, now known as *Spoletto*, whence its name; the best umbers, however, hail from Cyprus but are known in the trade as Turkey umbers since they were originally shipped from Constantinople, their real source being at the time unknown. Sienna was likewise first found near an Italian town bearing the same name. Both ochres and umbers are found in this country—Cornwall, Derbyshire, and Oxfordshire—in Wales, Italy, France, Australia, and the New World.

The methods of preparing these natural deposits for the use of the painter vary somewhat according to their source. The ochres are first ground if they are hard, but this process is omitted if they are soft. They are then levigated, or mixed with water and allowed to settle in large tanks. The coarser particles obviously fall to the bottom first, and if the supernatant liquid is poured off, and again allowed to settle, the sediment will this time be considerably finer. Repetition of this process for some four or five times will clearly yield a pigment of very varying grades of quality. It is usually found that the depth of colour of the ochre varies considerably according to the degree of fineness, the finest ochres being the palest. The sediment obtained in this way contains about 50 per cent. of water and is dried by the aid of gentle heat. If the temperature is allowed to rise too high the ochres develop a ruddy hue owing to their partial conversion into the anhydrous oxide, known as rouge or red oxide.

Umber is frequently sent into the market direct from the mine without any treatment. It is then known as ordinary "raw umber." If it is first levigated it is styled "powdered raw umber." Sienna is not usually levigated, but it may be ground if necessary. These pigments are very inert from a chemical point of view, and are therefore characterised by their durability and permanence. Somewhat similar pigments to the above are **Vandyke brown** and **Cappagh brown**. The former received its name in honour of the great painter who is known to have been particularly attached to the liberal use of browns, whereas the latter is from the district in Cork, Ireland, where it is mined. Vandyke brown contains a fairly high percentage of organic matter, and is greatly prized on account of its transparency, which enables it to be painted over the surface of other pigments, producing beautiful tones. According to Church (*q.v.*, p. 206) Cappagh brown contains approximately 27 per cent. of manganese oxide.

**Rouge.**—Mention has already been made of the fact that, if the ochres are overheated during the drying process, they are converted more or less completely into **rouge**, the anhydrous oxide of iron,  $\text{Fe}_2\text{O}_3$ , owing to the expulsion of the combined water of hydration. This is one of the methods by which the various red iron oxide pigments are prepared. The ochre is heated in specially constructed furnaces for varying lengths of time or at different temperatures according to the particular depth of colour required. The resulting products are known variously as **Indian red**, **Venetian red**, **Red oxide**, **Rouge**, etc. In a similar manner sienna and umber yield **Burnt sienna** and **Burnt umber**.

The anhydrous oxides of iron are also prepared by calcining ferrous sulphate or copperas,  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ , obtained by the atmospheric oxidation of iron pyrites ( $\text{FeS}_2$ ) in the presence of moisture and scrap iron. The changes taking place during the weathering may be represented as follows:—



and during calcination:—



A third method of preparing the anhydrous oxides of iron is afforded by the fact that in many manufacturing processes large quantities of iron salts are produced as waste products. From these the brown hydrated ferric oxide is precipitated by



the addition of alkali (soda, ammonia, or lime) and heated to redness in crucibles in a similar manner to the ochres.

These red oxides are very valuable pigments, being characterised by their inertness and permanence. They do not mix so well with oil as red lead, neither do they act as driers. They are particularly valuable in the preparation of paints for the coating of iron work and the like. The Maori use a variety of rouge for decorative purposes under the name of *Kokowai*.

**Terre verte** is a green earthy pigment found in the Mendip Hills, and in several other European countries. It consists essentially of silica and oxide of iron, small quantities of other oxides being usually present as well, together with from 6-8 per cent. of water.

**Siderin yellow** is a basic chromate of iron, and finds a limited application as a water colour. It is prepared by heating solutions of ferric chloride and potassium bichromate.

**Prussian blue** (p. 559), known to the chemist as ferric ferrocyanide,  $\text{Fe}_4(\text{FeC}_6\text{N}_6)_3$ , was discovered accidentally by Diesbach, a German colour manufacturer, in 1710. It is characterised by its intense colour, a single pound of it sufficing to give a perceptible tinge to over 600 lbs. of white lead. It is prepared by adding potassium ferrocyanide (yellow prussiate of potash) to a ferrous salt which has been oxidised to the ferric condition with bleaching powder. Obtained in this way the pigment is known as **Chinese blue**. Commoner makes enter the market as **Prussian blue**, **Berlin blue**, **Paste blue**, etc., and ordinary alum is one of the ingredients used in their preparation. In manufacturing **Antwerp blue** both alum and zinc sulphate are employed. **Brunswick blue** is an admixture of Prussian blue with barytes and silica or some other insoluble white pigment. The great drawback to the use of this composition is the tendency exhibited by the heavy barytes to settle to the bottom, the blue remaining suspended in the supernatant oil.

Prussian blue is unusually difficult to grind in a drying oil owing to a curious tendency to "leather" or "liver," that is, to set up to the consistency of leather. This difficulty is usually overcome by paint grinders by the use of special mixtures or blends of oil in which this peculiarity is shown to a minimum extent. Being insoluble in dilute mineral acids, Prussian blue is very permanent in certain acid atmospheres. Alkalis, however, readily decompose it, forming red ferric hydroxide. Warming with oxalic acid solution effects its solution, the resulting liquid being used extensively at one time as an ink. More recently, however, aniline dyes have tended to replace this older product. When used as a water paint, Prussian blue fades slowly on exposure to light, but the colour returns to its original intensity after prolonged darkness. Owing to its intense staining properties, Prussian blue is seldom used alone. Mixed with barytes and chrome yellow the so-called **Chrome greens** or **New Brunswick greens** are produced, which possess good body and colouring power, and work well both in oil and in water. When the chrome yellow in these pigments is replaced by zinc chrome, the so-called **Zinc greens** are produced. These are very popular on account of their relatively low cost and their brightness. An astonishing variety of hues, tints, and shades can be produced by suitably adjusting the proportions of their several constituents, which is a great advantage. Zinc greens are more apt to "run" or "blue" than the chrome greens, and they possess a slightly inferior body. On the other hand they are more permanent, since zinc chromate itself is more stable than chrome yellow.

**Armour-scale Paints** form a numerous and very variable class of grey paints. They all consist mainly of micaceous iron ore, generally admixed with the common red oxide of iron and gangue, and more or less graphite. There should be no rosin, rosin-oil, driers, or turpentine present. The colour of these paints is very variable, though it is generally some shade of grey. The specific gravity also varies considerably; it is, however, higher than that of graphite or silica-graphite paints, and lower than that of most other paints.



**Smalt** is a potash glass containing oxide of cobalt instead of lime. It is prepared by mixing zaffre (the technical name for cobalt oxide) with powdered quartz and potassium carbonate, and subjecting to a white heat in clay crucibles. On throwing the fused mass into water, disintegration into small angular pieces takes place. These are ground, levigated, and dried. Although very permanent, the colouring power of smalt is weak. This defect, together with its cost, has decreased its popularity amongst painters of late years.

**Cobalt blue** is prepared by heating to redness the precipitated oxides of cobalt and aluminium, and is used largely by water-colour artists. Its extreme permanence and resistance to the attacks of acids and alkalis have caused it to be used for superior decorative purposes.

**Cobalt green** is similar to cobalt blue, zinc oxide taking the place of alumina. It is also known as **Rinmann's green** and **Zinc green**, but its use is limited owing to its cost.

### Pigments Containing Copper

With the exception of copper chromate, the copper pigments are possessed of a green or blue colour, and were for many years highly prized. They are not very permanent, however, and are all blackened by sulphuretted hydrogen, owing to the formation of black copper sulphide  $\text{CuS}$ , which renders their use subject to the same limitations as the lead pigments. Moreover, many of the pigments are blackened by heat owing to their decomposition to black copper oxide.

One of the most interesting of the copper pigments is the basic acetate, popularly styled **Verdigris**, and which is manufactured in several ways. The old French method consists in exposing scrap copper to the action of grape skins discarded from the vineries. These skins, on fermenting, produce acetic acid which attacks the copper, converting it into the acetate. After two or three weeks sufficient verdigris has formed to be worth scraping off. The greenish blue colour of verdigris is familiar to all. In oil it is usually more permanent than in water. When strongly heated, black copper oxide results, so that due care must be exercised in drying the pigment. It dissolves readily in dilute acids without effervescence. Should an evolution of gas occur, the presence of some carbonate impurity is to be suspected. If a white residue remains, barytes, silica, etc., are probably present. Should the residue be blue, the probability is that Prussian blue is present; confirmation is afforded if the mass becomes brown on addition of caustic soda (see **Prussian blue**, above).

**Lime blue** is essentially a mixture of calcium sulphate and copper hydroxide, and is prepared by adding milk of lime to a solution of copper sulphate containing excess of ammonia. Some years ago, before ultramarine could be prepared in a cheap way artificially, lime blue was in great demand for frescoes and colour washing. In common with all copper and lead pigments, however, it is discoloured by contact with sulphur, and may not, therefore, be mixed with such bodies as cadmium yellow, ultramarine, and the like.

**Scheele's green** is now antiquated, and rightly so, on account of its poisonous properties, being a compound of the oxides of copper and arsenic. **Emerald green** is an aceto-arsenite of copper, and may be prepared by mixing equal quantities of white arsenic and verdigris with water, and allowing to stand. Other names for this pigment are **Paris green** and **Schweinfurth green**.

A basic carbonate of copper is found as the mineral **malachite**,  $\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$ , in Cornwall, Yorkshire, and other parts of Great Britain. When finely ground it is used as a pigment under the names of **Mineral** or **Mountain green**. **Azurite**



is another basic carbonate of copper to which the formula  $2\text{CuCO}_3 \cdot \text{Cu}(\text{HO})_2$  is usually given. This yields the **Mountain blue** of the painter.

**Bremen blue** is an artificial product obtained by intimately mixing copper carbonate with an excess of copper hydroxide. **Blue verditer** is a basic carbonate of copper, prepared by mixing together solutions of copper sulphate and sodium carbonate. It is used by water-colour artists to a limited extent, but is not very permanent. The so-called "Refiners' Blue Verditer" is just the same thing, but has been prepared from copper solutions obtained in the refining of silver and gold—hence its name.

**Old Brunswick green** was, strictly speaking, a basic chloride of copper, now rarely manufactured. The term, however, is misleading, both Emerald green and Bremen blue being known by this name as well.

**Copper chromate** is a brownish red pigment prepared by the action of potassium chromate upon a soluble copper salt. It is seldom used.

### Pigments Containing Aluminium

Metallic aluminium, usually mixed with zinc, in the form of a fine powder is frequently used as a pigment for painting iron work, and widely divergent opinions are held as to its value.

**China clay** or Kaolin is a silicate of aluminium to which the formula  $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$  is given, and is formed in nature by the weathering of felspar, itself a decomposition product of granite. It is found in Cornwall and receives extensive application in the manufacture of "china"—whence its name.\* It is used largely in distemper work, and owing to its cheapness is rarely adulterated. As an oil pigment it is a failure, since it loses much of its body when mixed with oil.

The only other pigment belonging to this group is **Ultramarine**, which has for centuries enjoyed a world-wide reputation amongst painters. Originally it was obtained from the rare mineral "lapis lazuli," the sapphire of the ancients, which is found in small quantities in Persia, China, Siberia, and South America. The price, however, was prohibitive, the pigment being listed at eighty shillings per ounce a century ago. At the present time ultramarine is manufactured in two ways, designated as the Direct and the Indirect methods respectively.

#### a. The Direct Method.—A finely ground mixture of—

Kaolin	-	-	-	-	-	-	-	31.5
Sodium carbonate	-	-	-	-	-	-	-	28
Sulphur	-	-	-	-	-	-	-	34.5
Charcoal	-	-	-	-	-	-	-	6
								<hr/>
								100

is heated for several hours at a bright red temperature. On cooling the burnt mass is removed, ground, and levigated. The finer qualities are used in different kinds of printing, the coarser being reserved for the painter.

b. The Indirect Method is conducted in two stages, comprising calcination and "colouring." The actual constituents of the mixture to be calcined depends upon

\* White pottery was imported from China before kaolin was known to occur in the British Isles, and was called "china" in consequence. When kaolin was discovered in Cornwall and was used for making similar white pottery it received the name China clay.



the nature of the product required. Thus, for sulphate ultramarine the following mixture is used : \*—

	I.	II.	III.
Kaolin - - - - -	50	47	26
Sodium sulphate - - - - -	41.5	19.5	57
Coal - - - - -	8.5	8	...
Sodium carbonate - - - - -	...	19.5	...
Sulphur - - - - -	...	6	8
Rosin - - - - -	...	...	9
	<hr/> 100	<hr/> 100	<hr/> 100

For soda ultramarine rich in silica :—

	I.	II.
Kaolin - - - - -	33.0	33.3
Silica - - - - -	3.5	...
Sodium carbonate - - - - -	36.5	30
Sulphur - - - - -	22.5	33.3
Coal - - - - -	4.5	1.3
Rosin - - - - -	...	2
	<hr/> 100	<hr/> 100

For soda ultramarine poor in silica :—

Kaolin - - - - -	36.5
Sodium carbonate - - - - -	36.5
Coal - - - - -	4.5
Sulphur - - - - -	22.5
	<hr/> 100

One or other of these mixtures is heated for from seven to ten hours in a furnace, after which it is washed and ground as finely as possible to assist in the extraction of all the soluble matter. This product is known as **Green ultramarine**, and is used by water-paint manufacturers, constituting **Lime green**. In order to convert this green product into blue ultramarine, it is heated again, this time with sulphur. On cooling and grinding the pigment is ready for the market.

What the chemical changes may be which take place during these operations is very uncertain, and until they are understood better we can scarcely hope to discover a more satisfactory method of preparing the pigment.

As a pigment ultramarine is fairly stable, particularly so in contact with alkali, and thus forms a marked contrast to Prussian blue. It is, therefore, used largely in the colouring of distempers, etc., for which Prussian blue is obviously unsuited. Acid soon attacks it, however, liberating sulphuretted hydrogen. For this reason, pigments containing lead or copper may not be safely mixed with ultramarine, as darkening is sure to occur.

### Pigments Containing Carbon

Carbon is largely used as a pigment owing to its remarkable permanence and inertness. **Carbon black** or **Charcoal black** is made by heating wood in closed retorts to a high temperature, the resulting mass being ground and washed. **Frankfurt** or **Drop black** is prepared similarly from vine twigs, bones, ivory, etc. The ground carbonised product is mixed with glue water and sent into the market in the form of tears or drops—whence the name, “drop” black. **Ivory black** should be made only from ivory cuttings, but the pure pigment is rare, owing to the high cost of ivory. **Animal black** is prepared by carbonising all kinds of animal matter (leather, horn, hoofs, skin, etc. etc.), and its composition is in consequence subject to variation. In the preparation of **Bone black**, animal bones alone are supposed to be used.

\* See p. 78, “Introduction to the Chemistry of Paints,” by J. Newton Friend (Longmans & Co., 1910).



**Lampblack** contains the highest proportion of pure carbon, and is a valued pigment. In order to prepare it heavy oils are heated in a pan, and afterwards ignited in a limited supply of air. The soot is collected in suitable chambers divided into series of compartments by partitions, and at regular intervals workmen enter the chambers and scrape away the pigment. A yield of 30 per cent. is regarded as satisfactory. A variety of lampblack bound with size and containing small quantities of camphor, musk, and possibly sepia, is known as **Indian ink**. The method of manufacture, however, is kept secret.

A complete analysis of the carbon blacks would be very difficult to effect, and is seldom required. The free water is usually estimated by heating a portion of the pigment in a steam oven (or hot-air oven at  $110^{\circ}\text{C.}$ ) until constant in weight. The residue is ignited in a crucible until only a whitish ash remains, and the percentage of volatile carbonaceous matter and non-volatile ash calculated from the results. Such an analysis is sufficient for most purposes.

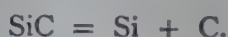
**Graphite paints** are chiefly used for the protection of iron and steel structures. They are usually of a grey colour, but are sometimes toned up by red lead, iron oxide, or other highly coloured pigments, thus giving red, brown, or green shades. These paints may be divided into graphite, silica-graphite, and armour-scale paints.

Graphite paints are generally made from naturally occurring graphite ores containing iron oxide, alumina, silica, etc., the percentage of graphite varying from about 25-45 per cent. They are heated to expel the water which is always present to a small amount and then finely ground. They are then ready for use.

An artificially prepared graphite has recently been introduced under the name of "Acheson graphite." This is prepared by heating anthracite coal and sand for several hours in an electric furnace. The silica (sand) is first reduced to silicon, which then unites with excess carbon to form silicon carbide or carborundum. Thus:—



As the temperature is raised the silicon carbide dissociates, the silicon volatilising and leaving the carbon behind in the form of graphite. Thus:—



The advantage of this process is that the graphite obtained is exceptionally pure, since at the temperature of its formation all impurities volatilise. The product is broken up and graded. That used for the manufacture of paint is ground to an extremely fine powder, and air floated for collection.

Graphite paints have a soft grey tint—when left of the original colour—and are of very low specific gravity. They are readily adulterated—especially by means of steatite—and are sometimes found to contain no graphite at all.

Silica-graphite paints vary greatly in composition. They should consist of a mixture of graphite and silica, but are frequently adulterated with steatite, barytes, furnace-slag, red lead, iron oxide, etc., in the same manner as graphite paints. These paints closely resemble graphite paints in colour and specific gravity.

### Pigments Containing Barium, Strontium, Calcium, and Magnesium

One of the most important of these is **Barium sulphate**, known variously as **barytes** and **permanent white**. It is characterised by its extreme insolubility in all the ordinary reagents, acids and alkalis having no effect upon it. It may easily be prepared by adding dilute sulphuric acid to solutions of any soluble barium salt. Barium sulphate occurs in nature as the mineral **barytes** or **heavy spar**. These are crushed and washed in the usual way. As iron compounds are not infrequently present, the crushed ore is usually treated with acid which dissolves out the iron, but leaves the barytes unattacked. Barytes possesses inferior body to white lead, but it mixes well with oil. A particle of the substance held on the end of a platinum wire, moistened with strong hydrochloric acid and introduced into the tip of a Bunsen flame, imparts to the latter a characteristic yellowish green hue. By means of this test the presence of barium salts may readily be detected.



**Calcium sulphate** is used as a pigment under the names of **Terra alba**, **Mineral white**, etc. As **Gypsum** it occurs in many parts of England, and this, when ground, yields a very durable and useful pigment. Mixed with hydrated aluminium oxide, the so-called **Satin white** is produced, which possesses superior body. Calcium salts impart a red colour to the Bunsen flame. **Strontium sulphate** is very similar to gypsum, and is occasionally used as a pigment under the name of **Strontian white**.

**Barium chromate**, variously known as **Barium chrome**, **Lemon chrome**, and **Yellow ultramarine**, is prepared by acting upon a soluble barium salt with potassium chromate. Thus:—



Potassium bichromate cannot be used, otherwise the barium salt is kept in solution by the free acid, thus:—



Barium chrome has a pale yellow colour, which is very permanent. It is not often used as a pigment, however, being too pale for most purposes, and lacking in body.

**Calcium carbonate** is better known to the painter as **Whiting**, **English white**, **Spanish white**, and **Paris white**. It is seldom used as an oil colour, partly because it assumes a dirty grey shade, but principally because its lightness and porosity cause it to absorb so much oil that its opacity is almost lost. Mixed with linseed oil it yields putty. **Gilders' whiting** is simply a superior quality of whiting. **Magnesite**, the carbonate of magnesium, is occasionally used as a pigment.

### Pigments Containing Zinc and Cadmium

**Zinc oxide** is now being used by painters with increasing favour under the names of **Zinc white** and **Chinese white**. It is manufactured from metallic zinc, which is thrown into white-hot retorts made of fireclay. The vapours issuing from the mouth of the retorts are caught in a current of air and burn with a smoky flame, the fumes being collected in special chambers and used direct as a pigment. A similar method is in use for the preparation of zinc oxide direct from the ore without necessitating the isolation of metallic zinc, which is a costly process. It is stated that 85,000 tons of the pigment, containing over 98 per cent. of zinc oxide, are now being manufactured in the U.S.A. in this way.

When of good quality, zinc white is very pure, fine, and easily worked. Being quite insoluble in oily water and turpentine, it is gradually replacing white lead for many purposes, for it is not so poisonous, and is permanent in the presence of fumes and pigments containing sulphur, in which circumstances white lead is rapidly discoloured. Owing to its cost, zinc oxide is liable to adulteration. Any impurities, however, are readily detected. The pigment is warmed with dilute sulphuric acid. *If pure it should dissolve completely to a colourless solution without effervescence.* This is perfectly characteristic. If effervescence occurs the presence of a carbonate is to be suspected. Should an insoluble residue be left, the presence of silica is to be inferred or some compound of barium, calcium, or lead, which was either present as the insoluble sulphate, or has been converted into such by the sulphuric acid added.

**Zinc chromate**, **Zinc chrome**, or **Citron yellow** is prepared by precipitation from solutions of its soluble salts with potassium chromate. Thus:—



The solutions must be neutral, and potassium bichromate cannot be used for the same reason as in the preparation of barium chrome (*q.v.*).



Zinc chrome is used very largely in the manufacture of zinc greens (*vide supra*). Since zinc sulphide is white and not black, zinc chrome is not seriously discoloured by contact with pigments containing sulphur, and in this respect is superior to the corresponding lead chromate—chrome yellow (*q.v.*). It is frequently adulterated with lead chromate, the presence of which may readily be detected by the black colour produced on addition of water containing sulphuretted hydrogen.

Zinc sulphide is rarely used as a pigment alone, but mixed with barium sulphate the well-known **Lithophone** or **Lithopone** is produced. This is used solely as an oil colour, and seems to be regarded with considerable favour by painters generally. Lithopone turns grey in sunlight, and so is unfitted for painting exteriors.

Cadmium sulphide appears in the market as **Cadmium yellow**, and when pure is a most permanent pigment. It is not often adulterated. Admixed with white lead, the so-called "brilliant yellow" is produced. This combination is very unsatisfactory, however, for the white lead gradually discolours owing to the formation of black lead sulphide.

### Pigments Containing Chromium and Manganese

The only compound of chromium which it behoves us to consider in this section is the oxide  $\text{Cr}_2\text{O}_3$  known variously as **Chrome green** and **Guignet's green**. Of these terms the latter is the better, as the former is frequently used for designating the greens produced by mixing lead chromate and Prussian blue (*q.v.*). Guignet's green is usually prepared by fusing a mixture of boric acid and potassium bichromate. On cooling, the mass is washed and ground, yielding an extremely permanent and very beautiful pigment.

**Manganese dioxide** occurs in nature as **Pyrolusite**, and is occasionally used as a black pigment under the name of **Manganese black**. Owing to its expense, relatively to the carbon blacks, and its powerful drying properties, its use as a pigment is greatly curtailed.

### Pigments Containing Arsenic and Antimony

**Arsenic sulphide** or **King's yellow** occurs free in nature as the mineral **Orpiment**, the "*auri pigmentum*" of the Romans—whence its name. Owing to its poisonous properties it is not now held in great favour. **Antimony sulphide** or **Antimony vermilion** is very similar in its properties, but these two pigments have been largely superseded by the chromes.

### Pigments Containing Mercury

The only pigment belonging to this group that demands our attention is **Vermilion** or mercury sulphide, which has been regarded with great favour from very early times. The Egyptians are known to have used it 400 years B.C., and it was greatly prized by the Greeks and the Romans. In those times, however, the pigment was obtained by grinding the mineral **cinnabar**, which occurs in China, Japan, Austria, Spain, and the New World. At the present time, vermilion is prepared exclusively from the artificial product.

One of the earliest methods of manufacturing vermilion is that known as the Dutch Process, and is effected in two stages. A mixture of mercury and sulphur is gently heated in an iron pot, whereby combination gradually takes place, and black mercuric sulphide results. This mixture, which is known technically as "ethiops," has now to be "coloured." To this end it is thrown in small quantities



at a time into red-hot earthenware crucibles fitted with lids. After some thirty-six hours the crucibles are cooled, and the vermilion, which has sublimed to the lids and upper and cooler parts of the crucibles, is removed.

The Idrian method consists in thoroughly mixing 20 parts of sulphur with 105 parts of mercury in wooden barrels rotating some sixty times per minute for about three hours. The resulting mixture should not reveal any globules of mercury when examined with a lens. It is then charged into pear-shaped sublimation pots of cast iron, each of which holds 130 lbs., and is gently heated, whereby black mercury sulphide results. The temperature is now raised and the vermilion sublimes into receivers. It is ground in water, boiled with potash to remove any sulphur, washed, and finally dried at 70°-75° C. After sifting it is ready for the market.

The Chinese process is very similar to this, and if the Chinese vermilion is superior to the European product it is probably because more care is taken by the patient Chinaman in carrying out the minor details of the process.

Vermilion has a beautiful scarlet hue, which is probably the result of its crystalline structure, for when mercury sulphide is first produced, either by precipitation with sulphuretted hydrogen from solutions of soluble mercury salts, or, as in the above case, by heating the mercury and sulphur together, it is always black and presumably amorphous. It would seem that vermilion exhibits a certain tendency to revert to its black amorphous form if exposed to the action of light, air, and moisture; so that as a water-colour pigment it is not very satisfactory. In oil, however, and particularly under varnish, vermilion is a very stable pigment in most cases. Owing to its unusual density (viz., 8.2) it is apt to settle out of paints, which latter must therefore be constantly stirred during application.

When heated strongly vermilion completely volatilises and should leave less than 1 per cent. of ash. Adulteration is often practised, red lead and rouge being added to it. Their presence, however, can readily be detected both qualitatively and quantitatively by heating the vermilion to redness in a crucible and examining the ash left behind.

**Statistics.**—The following figures show the amount of the English import and export of pigments:—

	Import, 1910.		Export, 1910.	
	Cwt.	Value.	Cwt.	Value.
Painters' colours and pigments: barytes -	908,505	£134,639	229,894	£38,118
" " " nickel oxide	17,297	86,150	23	235
" " " white lead -	288,731	240,372	404,401	401,897
" " " zinc oxide -	304,183	323,937	38,221	44,595
" " " other sorts -	860,304	786,167	1,692,465	2,208,460
Total of painters' colours and pigments	2,379,020	£1,571,265	2,365,004	£2,693,305

The United States imported in 1910 paints, pigments, and colours to the value of \$1,915,000. The export in 1910 was:—

Carbon black, gas black	-	-	-	\$680,000
Zinc, oxide of	-	-	-	956,000
All other	-	-	-	3,090,000
Total	-	-	-	\$4,726,000

For modern statistics see Appendix III.



## LAKES\*

Lakes are compounds of inorganic bodies with organic colouring matter; and during the past few years increasing attention has been paid to their manufacture in consequence of the rapid progress made in the preparation of dyes from coal-tar products. Originally the organic dyes were obtained solely from natural sources, such as, for example, lac dye from the lac insect, cochineal from the *Coccus cacti*, alizarin or madder from the roots of the madder plant (*Rubia tinctorum*), and so on. Almost all of these colours are acidic in character, and yield lakes when neutralised or made to combine with those metallic oxides or hydroxides which are basic in character. On the other hand the artificial dyes prepared from coal-tar products vary so much from one another in their chemical behaviour that different methods have to be employed in manufacturing lakes from them as occasion requires.

Lakes are usually poor driers, but they are characterised by their transparent nature, which makes it possible to use them in glazing or toning in a similar manner to Vandyke brown (*q.v.*). By mixing with some colourless (white) and opaque body such as barytes and gypsum the lakes are likewise rendered opaque, and thus resemble our ordinary pigments.

## A. Lakes from Natural Colours

Lakes from natural colours may be readily obtained by simply mixing the dyes with basic metallic oxides or hydroxides in vats. The resulting products are both coloured and insoluble in water—two important qualities essential to pigments. From a theoretical point of view a true lake should resemble a true salt, in that it contains just sufficient of the base as will combine with the colouring matter and no more. In practice, however, it is customary to add excess of the base, with the result that the tint of the finished product is proportionately lighter. In this way a gradation of tints may be obtained.

The most famous and important of the natural colour lakes is **carmine**, a compound of cochineal, lime, and alumina. The details of its manufacture are, however, kept a close secret. Carmine works satisfactorily both as an oil and a water colour, but fades on prolonged exposure to air and sunlight. During the preparation of carmine the metallic base does not effect the precipitation of all the cochineal, so the coloured liquors are mixed with alum, tin chloride, and potassium carbonate, the last named effecting the precipitation of the so-called **Carmine lake**. **Crimson lake** differs from carmine lake only in that it contains a higher percentage of alumina. **Scarlet lakes** are virtually crimson lakes tinted with vermilion.

## B. Lakes from Coal-Tar Colours

These are rapidly superseding those obtained from natural sources, as has already been mentioned. For our present purpose we may divide the coal-tar dyes into three classes as follows:—

1. **Acid Colours**.—This name is slightly misleading, for the acid colours are not necessarily of an acid character although such happens to be the case with some of them. The name "acid" colour originates from the fact that it is usual to add some free acid to the colour vats when dyeing wool and silk. The dyes are precipitated from solution by metallic salts; barium chloride, lead acetate, and aluminium sulphate being the three commonly employed.

Acid colour lakes may be used either as oil or water colours, and the results are very permanent. See also pp. 512 *et seq.* (Modern Pigmentary Dyestuffs).

\* For an account of the natural and artificial dyes now used by manufacturers for various purposes, the reader is referred to Sections XIII and XIV of this work, especially p. 443.



2. **Basic Colours.**—These yield precipitates with certain weak organic acids, such as tannic acid and picric acid. These precipitates are definite chemical compounds when pure, but in practice the relative amounts of the constituents are varied in order to effect corresponding changes in hue. Unfortunately the organic acids present exert a marked retarding action upon the drying of the oil used as vehicle, so that these lakes are not very suitable for oil paints. They are used as water colours, however, and good results are obtained by varnishing on top of such work.

3. **Mordant Dyes.**—These dyes are generally colourless, but when combined with a "mordant" their colour is developed. The actual colour developed depends very largely upon the character of the mordant used. Thus, for example, alizarin yields a scarlet colour with tin, a bright red with alumina, but a violet with iron.

The resulting lakes are usually very permanent.

## DISTEMPERS AND WATER PAINTS

**Distempers** are made by diluting cheap pigments with water containing a little glue to serve as a binding agent. They are applied to plaster, stucco, brick, and stone. In dry buildings they are very permanent. As a rule whiting is used in this country and coloured with small quantities of ultramarine, indigo, and such-like pigments which are characterised by deep staining properties. Sometimes the whiting is mixed with cheap permanent pigments, such as ochre and rouge, or indeed entirely replaced by these if a deep colour is desired. The pigments are made into a mud with water and size is added until the whole is of the consistency of cream. Occasionally alum is introduced into the mixture, but this is not to be recommended if pigments are used for staining which are susceptible to the action of alum. In America, lime preparations under the name of "Kalsomine" are used in distemper. Owing to the alkaline nature of whiting such pigments as Prussian blue, chrome yellow, etc., may not be used to colour it. The most suitable pigments for this purpose are ochres, umbers, siennas, rouge, lime blue, and indigo. These, alone and in combination, will suffice to yield a fine array of hues, tints, and shades.

The following table gives a list of foreign substances often added to distempers to modify their properties: \*—

Substance Added.	Result.
Turpentine } Paraffin }	Increased binding power.
Glycerin } Sugar } Treacle }	Slower drying.
Carbolic acid } Chloride of lime }	Deodorises and disinfects.
Vinegar	{ Neutralises the alkalinity of the lime. Renders size more fluid.
Alum	{ Renders size more fluid.
Spirits of wine	{ Size hardened and rendered less easy to remove.
Soap	{ Hinders undue absorption.

**Water paints** are not the same as distempers, although the two names are often regarded as synonymous. Water paints contain oil which has been saponified by treatment with alkali, and therefore yield non-absorbent coatings. A drop of water splashed on to these may be wiped off without leaving any mark. A distempered surface, however, would be temporarily darkened. Water paints are particularly suitable for walls, as they are porous and allow the bricks to "breathe." At the same time they are impervious to water and thus offer a good protection to the walls.

\* This table is taken from Friend's "Introduction, etc.," p. 148.



**Whitewash** and **Colour wash** are mixtures of lime and water, coloured in the latter case with cheap pigments. They are used in the interests of sanitation, rather than for decorative purposes.

**Casein Paints.**—It has long been known that the addition of casein (milk)\* to lime washes increases their durability, the reason being that casein combines with lime to form agglutinant compounds which become insoluble on exposure to air. Casein is now largely added to certain paints, usually supplied in the form of powder by the manufacturer, containing casein and alkali in the dry state. When these paints are mixed with water the alkali is dissolved, and in turn dissolves the casein, which then reacts with the lime and colouring matters to form coloured cements. In casein paints the cementing substances usually consist of casein ("curds"), quicklime, and water, but sometimes the casein colours are mixed with linseed oil varnish. The paints must be kept hermetically sealed in tins. Only mineral colours can be used. The paints are manufactured by adding 200 parts of casein with 40 parts of powdered quicklime, and the colouring matter is added until a thick paste is obtained, the mass being then finely ground in a colour mill. Casein paints give extremely stable colours with a matte surface and are very cheap.

## MODERN PIGMENTARY DYESTUFFS

Under this heading are discussed the principal types of synthetic organic pigmentary dyestuffs now commonly used in the paint and plastic industries as distinct from the inorganic pigments already described above.

The organic pigments show a far greater variety of shades than the inorganic pigments. They are superior in tinctorial power, brilliance of tone and softness of texture, but are inferior in covering power in most cases.

The ideal pigment should possess the following properties: Chemical inertness, light fastness, brilliance, insolubility, covering power, small particle size, good texture, low oil absorption and, of course, should be as cheap as possible.

The pigmentary dyestuffs used to-day may be divided into the following groups:—

- (1) Pure insoluble azo-pigments.
- (2) Toners.
- (3) Condensation and co-precipitation pigments.
- (4) Fanal type colours.

As mentioned under the azo-dyes group, (1) are generally manufactured by diazotising an amine and coupling with a naphthol or other phenolic group. The insolubility of the pigments obtained is due to the fact that neither the amine nor the naphthol contain solubilising groups such as sulphonic acids. An example of pure azo-pigments is **Helio red**—the couple product of diazotised *m*-nitro-*p*-toluidine and  $\beta$ -naphthol.

The toners are the metallic salts of soluble dyestuffs. Some examples are **Lithol red** barium and calcium toners, **Permanent red 2 B** and **Permanent red 4B** calcium and barium salts and the claret toners. Only one example will be given—that of lithol red which is a diazotised-2-naphthylamine-1-sulphonic acid  $\beta$ -naphthol couple product. The sulphonic acid group is the acid group which renders the dye active enough to form a barium or other metal salt, thus insolubilising the dye.

The claret toners give a useful range of maroons. In these, calcium or manganese, or mixtures of the two, render the  $\beta$ -hydroxynaphthoic acid group of the claret dye insoluble.

An example of the third group is **Helio marine blue GL**, which is prepared

\* See Industrial Casein, p. 79.

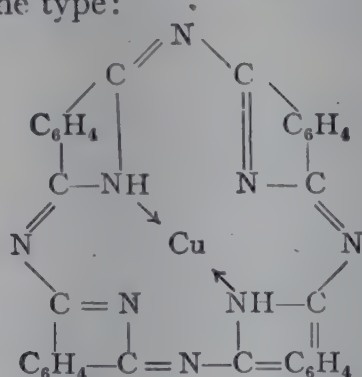


by condensing a basic dyestuff of the methylene blue type with an acid anthraquinone dyestuff.

The fanal dyestuffs are complex phosphomolybdotungstic pigments. These pigments are prepared by dissolving the basic dyestuff in water and running in the phosphomolybdotungstic acid or phosphomolybdic acid or whatever combination is required. The complex pigment is then precipitated. The triple salts give better light fastness.

These pigments are noted for their outstanding brilliance of tone and tinctorial power. Examples are **Rhodamine B** which is a magenta, and **Brilliant green** which is used for vivid green shades. Although we have mentioned these colours at the end of a section on pigments for paints they are not wholly satisfactory for paints and are generally used for printing inks. When used in paints delaking tends to take place with a reduction of light fastness but with an increase in the brightness of the shade. There are, however, certain points in favour of the use of fanal types for paints and further work is required with regard to their use in this way.

One of the most important types of pigmentary dyestuffs are those derived from the phthalocyanine range. The latter are made by roasting phthalonitrile with finely divided copper or copper oxide. Other methods are also adopted and other metals are used, principally magnesium. The formula of these compounds is thought to be of the type:



When copper is used **Phthalocyanine blue** is produced. **Phthalocyanine green** is obtained from this by direct chlorination in the presence of certain other agents. Twelve to sixteen chlorine atoms are introduced by this means.

Another favourite pigmentary dyestuff in the paint and cellulose industries is **Pigment scarlet 3B lake**. This is produced by coupling diazotised anthranilic acid with  $\beta$ -naphthol-3 : 6-disulphonic acid. This dye is dissolved in water and then precipitated as a lake by means of an alumina-blanc fixe base, often in the presence of sulphonated oils and zinc salts. This pigment is a very attractive geranium shade.

Particular properties required for pigments to be used in the paint industry are as follows:

The purity of the dyestuff intermediates is of extreme importance, for this determines the slight variations often observed in the same pigment from batch to batch, both as regards shade and weathering properties.

The stability of the pigment should be satisfactory when used in conjunction with other pigments and also when ground with oils such as linseed oil and driers such as the metallic naphthenates.

### Properties of the Pigmentary Dyestuffs and some of their Applications

**Pure Organic Materials.**—The Hansa Yellows are probably the most important range of yellow pigments. Examples are **Hansa yellow 10G** (**Irgalite yellow 5G**) and **Irgalite yellow G**. The former is a bright primrose yellow with excellent fastness to light and good tinctorial value. It is used in water paints, air drying and stove synthetic resins, cellulose and other plastics. In combination with a good blue, excellent greens are obtained. Irgalite yellow



5G is recommended for use in oil-bound water paints. It is non-poisonous. The shade is primrose, but slightly paler than 5G. Irgalite yellow G is a yellow chrome with great fastness to light and is very suitable for most applications in the paint industry.

The benzidine range consists of a number of yellows approximating to Hansa yellow in tone. There is also a very bright orange in this range. These colours possess the following properties:—

- (a) They have a semi-transparent tone.
- (b) They have a much stronger tinctorial power than Hansa yellows.
- (c) They have a high molecular weight and are consequently very sparingly soluble in oils.
- (d) They have a good heat stability.
- (e) Light fastness is fairly good.

These colours are used in the printing ink industry and in the rubber industry. Their use in the paint industry is growing. They are specially suitable for the lighter shades of stoving enamels.

**Benzidine orange** is used for shading the Hansa yellows for chrome shades.

**Dinitraniline orange** (Irgalite red 2G) has great permanency to light. It is not completely insoluble in the paint and printing ink oils but is satisfactory. It is especially used as a tinter for oil-bound water paints where it produces coral pink shades of excellent fastness. It has been found to be one of the most permanent organic pigments.

**Helio red** (Monolite red F, Scarlet RNS, or Irgalite red RN Extra) is a popular pigmentary dyestuff because of its brilliance, good light fastness and covering power. It has the advantage that the shade can be altered from yellowish to bluish by chemical and physical adjustments during manufacture. It is found to be suitable for oil and aqueous paints, but cannot be used for stoving enamels as it is volatile at high temperatures.

**Para red** (Irgalite red PR) is one of the oldest of the red organic pigments but is used in U.S.A. and Canada far more than in this country. Its main defects are only moderate fastness to light and a heavy bleed in linseed oil.

The above colours are all pure organic materials, and consequently it is not surprising that some are imperfect as regards insolubility in oils. The following group (toners) possess an inorganic part, usually a calcium sulphonate group, which imparts considerably greater insolubility in organic solvents.

**Toners.**—With the exception of **Lake red C** which is not light fast, there is a large range of toners for the paint industry. They are also used extensively by the plastics, rubber and printing ink industry.

The lithols and permanent red toners are bright and have high tinctorial power, good solvent resistance, good heat resistance and, consequently, behave very well in both air drying and stoving enamels. The calcium toner of **Permanent red B** is extremely light fast.

The claret toners are a range of extremely bright maroon shades. The calcium salt of Permanent red gives a claret while the manganese salt is a rich Bordeaux wine shade. They are used in both natural and synthetic paints and will withstand stoving at 270° F. They do not show excessive bleeding in the usual cellulose solvents.

**The Use of Pigmentary Dyestuffs in Paints.**—During manufacture, the surface of the dyestuffs is modified so that incorporation in the paint media is facilitated. Ease of incorporation is governed by the following factors:—

- (1) Dispersion.
- (2) Particle size.
- (3) Texture.
- (4) Oil absorption.
- (5) The pH of the medium.
- (6) The action of powerful solvents on the pigments.



In order to facilitate dispersion, wetting and dispersing agents are often used. (See section on Synthetic Surface Active Materials.)

### A Selection of Recent Patent and other Literature concerning the Paint Industry

*Conjugated Drying Oils.*—Lewis Berger & Sons Ltd. B.P. 14,575/1949. In order to remove the defect known as surface aberration, the dehydrated castor oil, oiticica oil, or tung oil is heated with a small quantity of an organic polysulphide containing the group  $>C-S-S-C<$  in the presence of a solvent (30 per cent.). The solvent should be a sweetened petroleum fraction of b.p.  $350^{\circ}$ – $500^{\circ}$  F. containing sulphur in the form of an organic sulphide which acts as a catalyst.

*Yields of Synthetic Alcohols.*—Standard Oil Development Co. B.P. 33,620/1948. This relates to the production of oxygenated organic compounds by the catalytic reaction of olefines, hydrogen and carbon monoxide in the presence of cobalt soaps. The important point of the patent is that improved yields are obtained.

*Particle Classification.*—Sharples Corporation. B.P. 10,598/1949. Relates to the classification of particles by passage into a vortex of air or, in general, a fluid. Particles withdrawn from the largest diameter of the vortex are larger than the selected critical size, while those withdrawn from the smallest diameter are smaller than the selected size.

*Styrene Copolymers.*—Monsanto Chemical Co. B.P. 5,364/1949. Relates to the production of styrene copolymers in which 30–45 per cent. of alpha-methyl styrene and 55–70 per cent. of styrene are reacted in aqueous emulsion (monomer to water ratio 0.1 to 0.5) in the presence of 0.1 to 0.5 per cent. of emulsion stabiliser. Yields approaching 100 per cent. are obtainable.

*Chemistry of Drier Action.*—C. A. Klebsattel, Advance Solvents and Chemical Corp., N.Y. Theories are given which account for drier action in film formation by polymerisation and association brought about by heat or oxidation, or both.

*Thermal Analysis of Metal Soaps.*—G. S. Hattiangdi, M. J. Vold, R. D. Vold (*Ind. Eng. Chem.*, 1949, **41**, 10, 2,320). The transition temperatures and approximate heats of transition based on differential heating curves for metallic stearates and palmitates are described.

*Correlation between Photochemical Reactivity and Chalking of Titanium Dioxide Pigments.*—A. E. Jacobsen (*Ind. Eng. Chem.*, 1949, **41**, 523–526).

*Water-paints.*—F. Margival (*Trav. Peint.*, 1948, **3**, 415–417). A discussion of the composition of water-paints and distempers based on glue. A. Iachan (*Rev. Quim. Industr.*, Rio de Janeiro, 1948, **17**, No. 200, 16–20). This article deals with the emulsion aspects of water-paints and the selection and treatment of raw materials, pigments, and their fabrication into paint.

*The Chemistry and Physics of Pigments.*—C. E. Barnett (*Ind. Eng. Chem.*, 1949, **41**, 272–279). A review is given of the surface chemistry and optical properties of pigments. The major advance during the last twenty-five years has been increased covering power. The composition of a number of pigments is also discussed.

*Methods for the Manufacture of Cadmium Sulphide.*—C. S. Schinetti (*Pitt. E. Vern.*, 1949–5, 23–27).

*A Continuous Chrome Yellow Process.*—R. Williams, jun. (*Chem. Eng.*, 1949, **56**, No. 3, 121–123).

*A New Nomenclature for Ferruginous Earths, Ochry Clays, Boles, and Ochres.*—H. Rabaté (*Trav. Peint.*, 1948, **4**, No. 8, 62–63).

*A Mechanism of the Oxidation of Drying Oils.*—P. O. Powers (*Ind. Eng. Chem.*, 1949, **41**, 304–309). Forty-one references are given in a discussion of the mechanism of the oxidation and subsequent polymerisation of drying oils. J. C. Cowen (*Ind. Eng. Chem.*, 1949, **41**, 294–304). Sixty-nine references are given in a review of the isomerisation reactions of drying oils.

*Chemical and Physical Explanations of the Metal Protective Nature of Red Lead.*—E. J. Dunn, jun. (*Paint Ind. Mag.*, 1946, **61**, 340, 342, 344–348).

*Recent Developments in Titanium Pigments.*—M. Schofield (*Paint Man.*, 1947, **17**, 386).

*Phthalocyanine Colours.*—A. H. Woodhead (*Paint Man.*, 1947, **17**, 369).

*Aluminium Flake Powders.*—G. W. Wendon (*Paint Man.*, 1947, **17**, No. 11, 373).

*Pigmentation and Pigment Manufacture.*—D. M. Stead (*J. Oil Col. Chem. Assoc.*, 1947, **30**, 337–350).

*Manufacture of Luminescent Zinc Sulphide Pigments* (I. G. Farben.).—L. C. Turnock and F. R. Lowdermilk (C.I.O.S.) 1945, Item 22, File XXIX., 14, 37–39.

*The Grinding of Pigments.*—D. E. Star (*Paint Man.*, 1947, **17**, 108–113). Factors affecting pigment dispersion are discussed. The use of wetting agents reduces the grinding time. Ball and pebble mills possess advantages, including low power consumption and maintenance costs.

*Comparative Tests on White Lead and Zinc Oxide Paints.*—A. V. Blom (*Verfkronek*, 1947, **20**, 143–145). Lead paints are considerably superior.

*Rheological Properties of Concentrated Dispersions of Solid Particles.*—J. S. Gourley (*XIth Int. Cong. Pure Appl. Chem.*, 1947. Author's Summary, 218/11).



*Modern Views on Drying Oil Chemistry.*—C. P. A. Kappelmeier (*Paint, Oil, Chem. Review*, 1947, **110**, No. 15, 5, 6, 30, 31). Oxidation, polymerisation, and isomerisation are discussed.

*The Use of Wetting Agents in Paints.*—G. A. Atkins (*Paint Notes*, 1948, **3**, 119-129). A bibliographical review of the mechanism of the pigment-dispersing action of wetting agents.

*Synthetic Iron Oxides and their Application in the Paint Industry.*—H. Zylbersztajn (*L'Ind. della Vernice*, 1947, **1**, 97-99). A review of the properties and uses of the yellow, red, brown and black pigments based on hydrated ferric and ferroso-ferric iron oxides.

*Reaction between Pigments and Emulsified Binding Agents.*—H. Wagner (*Farben, Lacke, Anstrichstoffe*, 1948, **2**, 17-19).

*The Use of Zinc, Aluminium, and Copper in Paints.*—A. Müller (*L'Ind. della Vernice*, 1947, **1**, 123-127). The rust inhibiting properties of aluminium paint are demonstrated.

*Green Earths.*—H. Rabaté (*Travaux de Peinture*, 1948, **3**, 172-173). Glauconite and celadonite.

*Modern Trends in Azo-colour Pigments.*—L. A. Melsheimer (*Amer. Paint J.*, 1948, **32**, No. 28, 84, 86). A short review of the structure and properties of the different classes of azo-pigments.

*The Anti-corrosive Properties of Zinc Chromate.*—T. Vignola (*L'Ind. della Vernice*, 1948, **2**, 2-5). A review of the chemical and physical properties of paints using zinc chromate are discussed, with special reference to their anti-corrosive properties.

*Cadmium Lithopone Colours.*—R. B. Quelos (*Paint, Oil and Chem. Rev.*, 1948, **111**, No. 8, 11-12). An account of the manufacture of the red and yellow cadmium lithopones.

*The Manufacture, Properties, and Analysis of the Cadmium Sulphide Yellow Pigments.*—U. Cuppini (*Pittura e Vernici*, 1946, **2**, 49-50).

*Background of Organic Pigments.*—L. S. Pratt (*Amer. Ink Maker*, 1948, **26**, No. 3, 32-33, 37, 57, 59).

*Properties of Lead Titanate.*—J. Rinse (*Paint Tech.*, 1948, **13**, 7-9). A review of the paint-making properties of lead titanate. Its merits are great opacity, low water absorption, gloss and elasticity retention on weathering and freedom from livering and hard setting on storage. Its defects are slow drying, necessitating the use of tung oil or alkyds, lack of resistance to mould growth and yellowish colour.

*Review of Patents on Lead Titanate.*—H. W. Bowron (*Paint Tech.*, 1948, **13**, 11-13).

*Modern Production of Barium Sulphide for Lithopone.*—A. G. Arend (*Paint Tech.*, 1948, **13**, 11-13). The use of coal and coke for the production of barium sulphide from barytes.

*Aluminium Flake Powders.*—G. W. Wendon (*Paint Man.*, 1948, **18**, 45-47). Describes the dyeing of aluminium flake powders to give a wide range of colours which can be used in paints. Golden shades on aluminium are preferred to metallic copper because of the greater resistance to aluminium to corrosion.

*The Effect of White Pigments on the Durability of Paint Films.*—E. J. Dunn, jun., and C. H. Baier (*Amer. Paint J.*, 1948, **32**, No. 52).

*Metal Soaps in the Paint Industry.*—E. Palmaer (*Füerg och Fern.*, 1948, **12**, 97-99).

*Glossary of Terms used in the Paint, Varnish, and Allied Trades.*—H. W. Chatfield (*Oil Col. Tr. J.*, 1948, **113**, 114).

*Modern Developments in the Production of Luminous Paints.*—H. Baum and E. R. Thews (*Paint Var. Prod. Mgr.*, 1948, **28**, 259-260, 262-266).

*Dispersion in Non-aqueous Media.*—J. L. van der Minne (*Verfkroniek*, 1948, **21**, 131-135).

*New Aluminium Paste Pigments.*—R. I. Wray (*Off. Dig. Fed. Paint Var. Prod. Cl.*, 1948, No. 281, 441-446).

*Aluminium Paints.*—G. Salomone (*Industr. Vern.*, 1948, **2**, 125-127).



## SECTION XVII

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Textile Fibre, Bleaching, and Waterproofing  
Industries





# TEXTILE FIBRE, BLEACHING, AND WATERPROOFING INDUSTRIES

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## PART I INDUSTRIAL FIBRES

### LITERATURE

- MITCHELL AND PRIDEAUX.—“Fibres used in Textile and Allied Industries.” London, 1910.  
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 H. A. CARTER.—“Ramie.” London, 1910.  
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 TROTMAN AND TROTMAN.—“The Bleaching, Dyeing and Chemical Technology of Textile Fibres.”  
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 HESS.—“Textile Fibres and their Use.” 1936.  
 HUNLICH.—“Textile Fibres and Materials.” 1940.  
 LEWIS.—“Introduction to Textiles.”  
 OAKLEY.—“Long Vegetable Fibres.”  
 SCHWARZ.—“Textiles and the Microscope.”  
 WARD.—“Textile Fibres and Yarns.”  
 MATTHEWS.—“The Textile Fibres: their Physical, Microscopical, and Chemical Properties.”  
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 See also under **Bleaching, Dyeing, etc.**

Two classes of fibres exist: (1) Vegetable, (2) Animal.

The former class consists essentially of cellulose (which see), while the latter consists of nitrogenous organic matter.

### Vegetable Fibres

**Cotton** consists of thin, hair-like fibres enveloping the seeds contained in the capsule of the cotton plant, *Gossypium*. According to Royle and Kuhn four fundamental species exist, each comprising many varieties. The bulk of the cotton comes from the Southern States of the United States of America; perhaps the best cotton comes from *Egypt*; cotton plantations also exist in various parts of Africa, East Indies, and other tropical or semi-tropical regions.

The cotton filaments consist of long, thin cellulose cells 1-5 cm. long and 0.04 mm. in diameter, forming flat, ribbon-like bands, twisted spirally and hollow internally. They may be likened to tubes which have collapsed in the interior, thus acquiring a dumb-bell-like section. This hollow twisted construction makes fabrics constructed of cotton both light and elastic.

The cotton fibres when freshly separated in special machines from the cotton seed consist principally of cellulose (91 per cent.), but are surrounded by a thin cuticle, and contain about 5 per cent. of non-cellulose constituents, such as resin, colouring matter, proteids, fats, etc., which are almost completely removed during the bleaching process. Commercial varieties contain about 8 per cent. of moisture. Dilute alkalis (under 10 per



FIG. 199.—Cotton Fibres, Enlarged.

cent.) scarcely affect cotton fibres, but more concentrated alkali solutions "mercerise" them. (See **Mercerisation**, p. 205.)

Both bleaching and mercerisation increase the affinity of the fibre for colouring matter.

Dilute acids in the cold also do not attack cotton fibres, but when warmed or evaporated to dryness with dilute acids the fibres fall to pieces owing to the formation of hydrocellulose (which see). Use is made of this fact in obtaining **shoddy wool** (p. 517). Wool, silk, and other animal fibres have a much greater attraction for dyestuffs than cotton. To remedy this, cotton is often "animalised" by treating with **casein** or other nitrogenous matter (e.g., milk + sodium stannate, then alum). Vignon and Cassella let  $\text{CaCl}_2 + \text{NH}_3$  act on cotton at  $60^\circ \text{C}$ . Ammonia is absorbed, and the fibres can be dyed in an acid bath without a mordant.

Prior to being woven into fabrics cotton yarns are "sized" (to render them softer, more pliable, and adhesive) by dipping into flour paste, dextrine, gum, or other adhesive, and adding kaolin,  $\text{BaSO}_4$ , etc. etc., as weighting agents. (See p. 561. See also **Mercerisation**, p. 205.)



**Linen** consists of fibres of the inner bark or bast of the **Flax** plant, *Linum usitatissimum*, largely cultivated in North Ireland, Belgium, and Russia. The plants are cut, freed from seed, and then, in order to separate the bast fibres from the ligneous portion, they are "retted," i.e., allowed to ferment in stagnant water contained in tanks. The woody tissues rot and the fibres are separated from them by beating, shaking, and other mechanical treatment. The fibres thus obtained are hollow, thick-walled tubes possessing a smooth polished surface tapering to a point at the end; they are 20-120 cm. long and 0.012-0.025 cm. broad. Linen fibres are stronger but not so elastic as cotton filaments; they are also better conductors of heat, thus explaining the cold feel attached to linen goods. Linen behaves with chemicals very similar to cotton; it is somewhat more inert to colouring matter and more easily disintegrated and injured by bleaching and oxidising agents than cotton; it contains 7-8 per cent. of moisture



FIG. 199a.

Linen Fibres,  
Enlarged.

**Hemp** is a fibre similar to flax, and is prepared in the same way from the hemp plant, *Cannabis sativa*. It contains more woody tissue than flax.

**Jute** is the bast fibre from several species of *Corchorus* (East Indies, India). The cut plants are 10-12 ft. in height and are made into fibre by retting. **Jute** consists principally of a compound of a tannic acid and cellulose which is called "bastose" and which is hydrolysed into its constituents by acids. Jute dyes with basic dyes much like wool.

**Ramie** is the fibre of China grass, belonging to the *Urticaceae* or nettle family.

**Cocoa-nut Fibre (Coir)** consists of the fibrous layer covering the shell of the fruit of the cocoa-nut palm, *Cocos nucifera*, which is cultivated in most tropical lands. It is used for cordage, and as a filling and spinning material.

**Sisal Hemp or Agave Fibre** is indigenous to Yucatan, and is largely grown in the Bahamas and in Florida. The leaves of the plant average 5-6 ft. in length, and are cut when four years old.

**New Zealand Hemp**, or *Phormium tenax*, resembles Manila, but is inferior in strength and quality.



**Manila Hemp** is obtained from the leaves of a plant of the banana family, and is largely cultivated in the Philippine Islands, Borneo, and Java.

**Esparto** is a grass, *Stipa tenacissima*, growing in Spain, Algeria, and Northern Africa. Much used for paper making, etc.

**Istle or Tampico Fibre** is made from a plant largely grown in Mexico, and used in very large quantities in the United States.

### Animal Fibres

**Wool** consists of the cleansed fibres of the sheep. The fibres vary in length from 2-25 cm., the shorter fibred varieties being termed "short stapled," "short wool," or "noils," and the longer ones, "long stapled," "long wool," or "tops." Long wools are manufactured into **worsted yarns**, while short wools go to make **woollen** or **carded yarns**. **Pulled wool** is separated from the skins of slaughtered sheep after a preliminary treatment with lime (which makes them difficult to dye). The fibres consist of a number of individual cells closely cemented together and overlapping so as to form a cylindrical solid curly fibre, covered with horny scales, which make the fibre look rough and uneven under the microscope.

The best and most expensive wool is given by the **Merino** sheep; wool is principally obtained from Australia, South America, and Africa; the crude wool as imported contains much sweat and fatty matter, which is extracted by washing, and gives the fat known as **Lanoline** (see pp. 53 and 60).

Wool consists of a substance called "keratine," which contains nitrogen (17.8-19.1 per cent.), sulphur (2.3-3.8 per cent.), carbon (49.8-52 per cent.), hydrogen (6.9-7.2 per cent.), and oxygen (20-21 per cent.). Boiling water causes the fibres to shrink up and mat together; warm alkalis decompose it, dissolving it to form fatty acids, amino acids, ammonium compounds, and sulphuretted hydrogen; weak bases, however, like ammonia, neutral soaps, and dilute acids, do not attack wool to any great extent. Bleaching powder, however, unless very carefully used, is liable to damage the fibre.

**Shoddy Wool**.—This consists of wool fibres recovered from old clothes and similar materials by a process known as "**carbonisation**." The old cloth is soaked in a dilute solution of dilute HCl, AlCl<sub>3</sub>, or MgCl<sub>2</sub>, separated from excess of liquor by centrifuging, and then is heated to 100°-125° C. The cloth consists of a mixture of vegetable and animal fibres; when heated the cellulose forming the vegetable fibres is attacked by the acid, forming the brittle hydrocellulose. On beating the cloth the vegetable fibres fall to dust and are thus easily separated from the interwoven woollen fibres which remain intact—wool not being very sensitive to acids.

Among other industrially important fibres chemically similar to sheep wool but smoother and less curly may be mentioned: **Alpaca** from the South American goat, *Auchenia paco*; **Vicuna** from the small South American goat, *Auchenia vicugna*; **Mohair** or **Angora** from the Angora goat; **Cashmere** or **Tibet wool** from the Cashmere goat, **Llama hair** from the *Auchenia llama*; **Camel hair**, **Cow hair**, **Horse hair**, **Goat hair**, etc.

**Silk** is the cocoon thread of the silk spinner, *Bombyx mori*, which is widely cultivated on mulberry trees in China, Japan, France, Italy, India, Asia Minor, etc. The spinning glands of the mulberry silkworm secrete two colourless liquids, which unite on issuing from the glands to form the yellowish double-thread known as silk. The worm winds the fibre around itself as an enveloping cocoon of length 400-1,300



FIG. 199b.  
Wool  
Fibre,  
Magni-  
fied.



yds., before passing into the chrysalis or pupil state. The chrysalis is killed by dry heat, steam at  $75^{\circ}\text{C.}$ , or by freezing, and the cocoons are then immersed in hot water to soften the silk glue known as **sericin** which forms the exterior layer of the filaments, and binds the strands together. The silk threads are then twisted on a reel to form the threads of **raw silk**. Only 50-66 per cent. of the silk in the cocoon can be reeled. The waste parts of the cocoon yield (after boiling with soda solution, combing, and spinning) the so-called "**floss silk**," which is made into **spun silk**. The waste from the spinning is sold as **silk wadding**.

Raw silk fibre consists of about 66 per cent. **fibroin**,  $\text{C}_{15}\text{H}_{23}\text{N}_5\text{O}_6$ , forming the real silk substance, and the silk gum or **sericin**, forming the exterior layers. To make the silk bright and lustrous the gum must be removed from the fibre by treating with hot, neutral soap solution, the strands being then washed with dilute sodium carbonate solution. The soap baths containing the dissolved gum are called "boiled-off baths," and are used in silk dyeing. Degummed silk is called "**Cuite**"; it is very lustrous and soft, but has lost 20-30 per cent. of its original weight. The "rustling" property of silk is attained by further treatment of the cuite in an acid bath. If the degummed silk is not to be dyed dark it is "boiled white" by sewing into coarse sacks, boiling with soap solution for thirty minutes, washing with  $\text{Na}_2\text{CO}_3$  solution and  $\text{H}_2\text{O}$ , bleaching with  $\text{H}_2\text{O}_2$  or  $\text{SO}_2$ , and again washing. Silk substance—both the sericin and fibroin—is rapidly dissolved by alkalis, zinc chloride, and cuprammonium; dilute acids do not attack it so readily. Silk is very hygroscopic, containing on an average 11 per cent. of water, and capable of absorbing nearly 30 per cent. without appearing damp. Consequently the estimation of the



FIG. 199c.—Silk Fibres.

water is of great importance in the silk trade, and is carried out in "conditioning" apparatus.

Several varieties of **Wild silks** are known, the most used being Tussore silk or Tasar silk, spun by the *Antheraea mylitta*, of a bright brown colour, very durable, and having a fibre thicker than that of genuine silk. Many of the wild silks are very difficult to properly bleach and dye.

For **Artificial Silk** see p. 219.

**Statistics.**—The following figures show the enormous value of the *import* of textile fibres into the United Kingdom :—

	Imported in 1910.	Value.
	Tons.	
Raw cotton, yarn, and waste - - - -	903,000	£72,760,000
Linen yarn - - - - -	14,400	1,050,000
Coir fibre and yarn - - - - -	3,200	250,000
Hemp (also tow and yarn) - - - - -	733,000	3,280,000
Jute (also yarn) - - - - -	298,000	4,720,000
Silk (including yarns, waste, etc.) - - -	4,900	1,880,000
Wool (including yarn, shoddy, and rags) -	500,000	40,120,000
		£124,060,000



The corresponding statistics for imports into the United States are :—

	Imported in 1910.	Value.
	Tons.	
Cotton (unmanufactured, waste and yarns) -	58,300	\$21,710,000
Flax - - - - -	12,761	3,536,000
Hemp - - - - -	6,423	1,040,000
Istle or tampico fibre - - - - -	9,272	645,000
Jute - - - - -	68,155	3,728,000
Manila - - - - -	93,253	10,517,000
New Zealand flax - - - - -	3,353	363,000
Sisal grass - - - - -	99,966	11,440,000
All other grass - - - - -	12,248	1,148,000
Coir yarn - - - - -	2,720	204,000
Human hair - - - - -	...	2,848,000
Horse hair - - - - -	2,410	2,107,000
Other animal hair - - - - -	5,960	1,065,000
Wool, camel hair, goat hair (unmanufactured)-	117,800	51,220,000
Silk (cocoon, raw, waste) - - - - -	10,470	67,129,000

The United States exports were :—

	Exported in 1910.	Value.
	Tons.	
Cotton (unmanufactured) - - - - -	1,431,600	\$450,447,000
Hair - - - - -	...	1,143,000
Silk waste - - - - -	1,200	64,000

For modern statistics see Appendix III.

## PART II

## THE BLEACHING OF TEXTILE FIBRES

## LITERATURE

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 KNECHT, RAWSON, AND LOEWENTHAL.—“Manual of Dyeing.” Vols. I. and II. London, 1910.  
 J. HERZFELD.—“Das Färben und Bleichen.” 3 vols. 1900–1910.

Textile fibres, either as yarn or woven into cloth, must undergo several preliminary operations before they can be passed on to the dyer and printer. By the process of “bleaching” heterogeneous matter in the fibre is largely destroyed or removed so that the cloth dyes equally in all parts.

**Cotton** is nearly always bleached by chemicals, usually by treating with caustic soda and calcium hypochlorite (bleaching powder) or sodium hypochlorite (prepared by the electrolytic process) solution. The caustic soda attacks the lignin and saponifies fats, dissolves resins, etc., while the hypochlorite completes the process by its strong oxidising action:— $\text{HClO} = \text{HCl} + \text{O}$ .

The cotton goods are sewn together in special machines so as to make a roll about  $\frac{3}{4}$ -1 $\frac{1}{4}$  yds. wide and sometimes 50,000 yds. long, and are then usually made to undergo the following series of operations:—

(1) *Singeing*.—They are passed through a singeing machine (Fig. 200) in which a gas flame plays on the cloth whereby the finer projecting fibres are burnt off. If

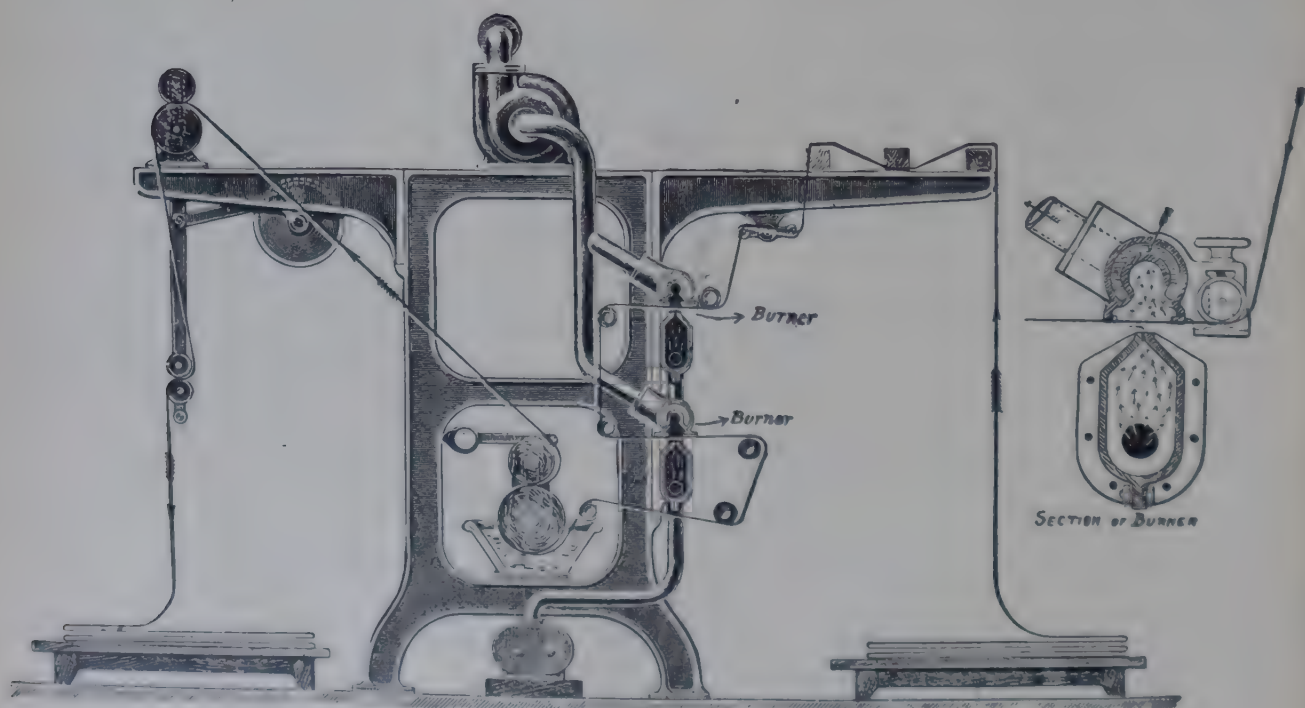


FIG. 200.—Gas Singeing Machine with Two Burners.  
 (Mather & Platt, Manchester.)



allowed to remain on these fine fibres would cause a smearing of the colours in printing.

(2) *Steeping or Souring*.—From the singeing room the goods are drawn in rope form through a porcelain ring ("pot's-eye"), and are treated with very dilute  $\text{H}_2\text{SO}_4$  in a *souring machine* (Fig. 201).

This consists of a tank filled with the acid solution and provided with wooden rollers; the hanks pass through porcelain rings (pot's-eye) into the acid bath, thence coming out, are squeezed free from liquor in a roller, and then pass again into the liquor, and are squeezed dry again, the process being

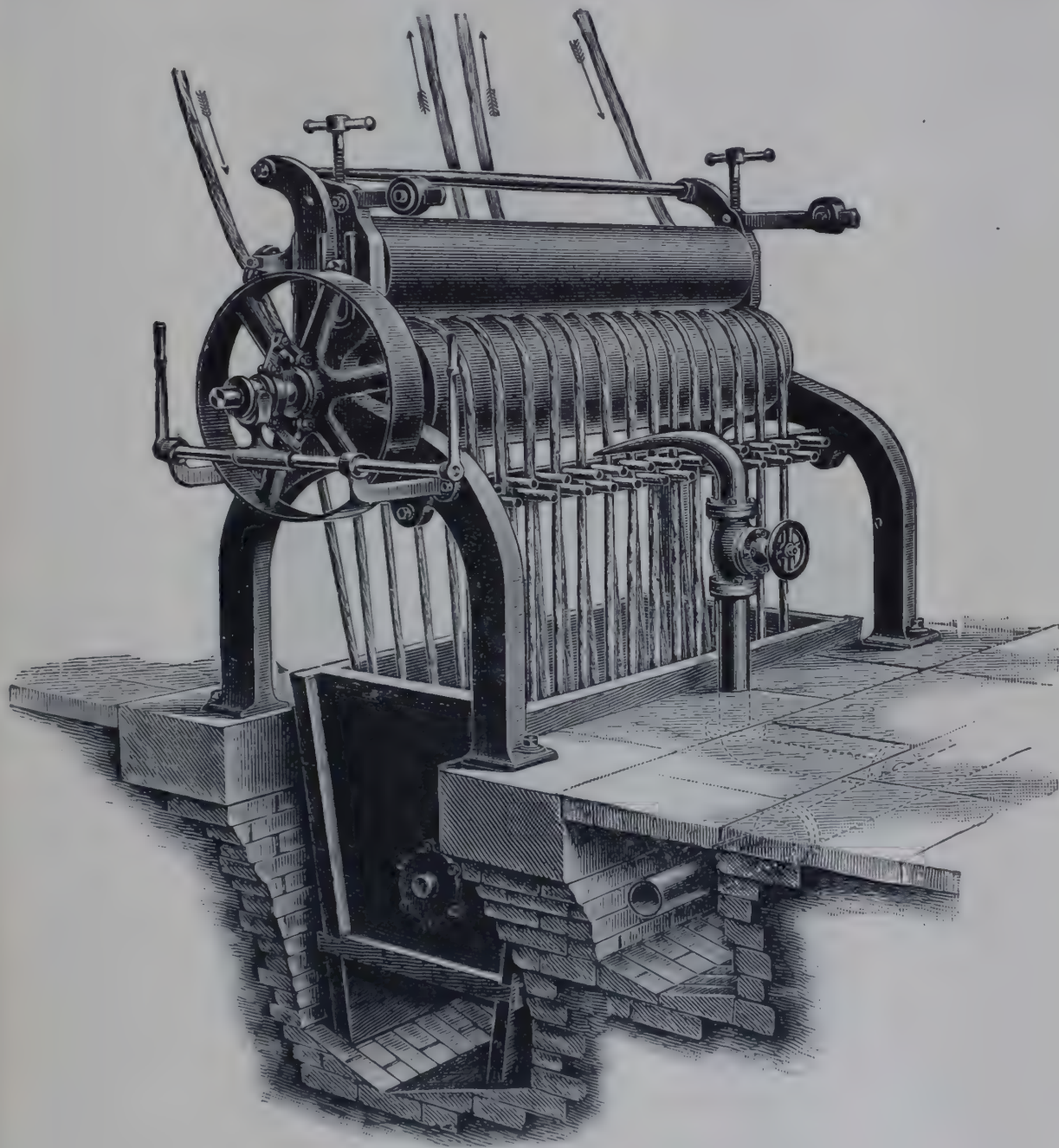


FIG. 201.—Souring and Washing Machine.  
(Mather & Platt, Manchester.)

repeated several times. After about twenty-four hours the acid completely hydrolyses all starch used for sizing the cotton and at the same time dissolves mineral impurities.

(3) The goods are then washed free from acid and mineral salts ("filling") in another similar machine. (4) The goods are next heated under pressure with dilute (3 per cent.) caustic soda in the autoclave—called a "Keir" ("bowking").

A diagram of Mather & Platt's apparatus is shown (Figs. 202 and 203). The goods soaked in caustic soda solution are placed in a perforated truck and run into the horizontal boiler (which is



capable of holding 1,270-3,400 kg. of goods) and the door mechanically shut. By means of an injection apparatus and centrifugal pump boiling caustic soda is forced in at the bottom, and caused to continually circulate through the goods, the heating being carried up to  $2\frac{1}{2}$  atmospheres for some hours, and being caused either by live steam coils placed in the bottom of the boiler, or by closed heating coils containing hot air or steam coming from an external source of heat. While one truck of goods is being treated the men are loading another truck externally, so that charging and recharging the apparatus takes little time. When the 3 per cent. caustic soda solution is pumped in at the bottom, all the air is driven out by steam. Unless all the atmospheric oxygen has been removed from the boiler the cloth may become rotten probably owing to the formation of oxycellulose. Vertical high pressure keirs are also used. Fig. 204 shows Farmer's high pressure kier.

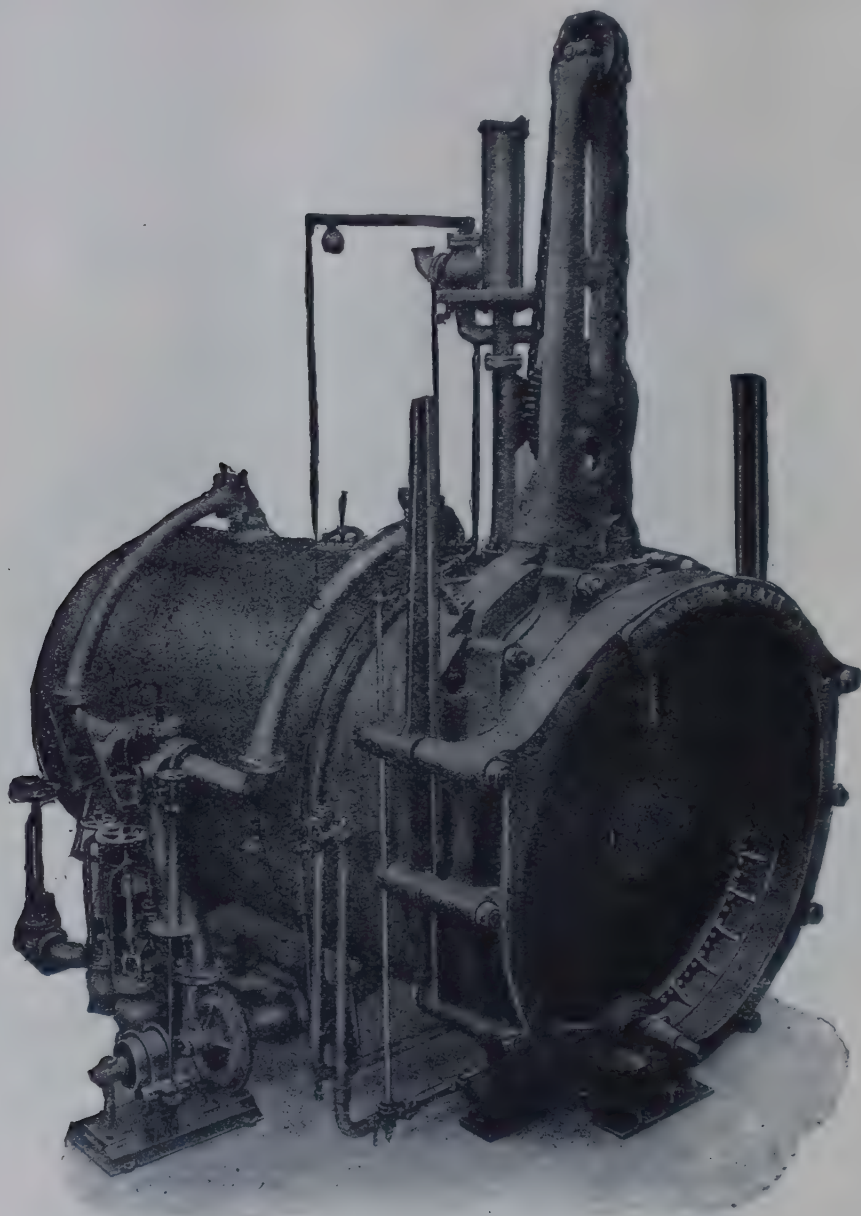


FIG. 202.—Mather Patent Keir (Full View).  
(Mather & Platt, Manchester.)

The goods are now almost white. After cooling they are (5) washed free from caustic soda, and then (6) *bleached* in large tanks with a dilute solution of bleaching powder (1 g. bleaching powder to 1,000 c.c. water). No acid is used, the goods being allowed to remain in the bleaching liquor for some time ("chemicing"). (7) Next the goods are washed, and the excess of chlorine and calcium salts removed by passing (8) through dilute acid followed by (9) a thorough washing.

(10) The cloth is now dried by passing over a series of steam-heated hollow copper rollers; (11) again passed through singeing machines to remove fine projecting fibres; (12) well beaten, and (13) rolled up, whence it goes to the dyers or cloth printers.



The succession of operations is often varied widely according to the goods and the purpose for which they are intended. Thus pieces to be dyed dark colours require a different treatment to those intended for lighter shades or white finishes.

Thus many firms work by the process of *double bowking*, viz., by boiling with lime first and soda or resin lye after, or by means of a strong caustic lye alone (*single bowking*). The souring and "chemicing" (*i.e.*, treating with bleaching chemicals) is done either in souring or "chemic" cisterns arranged with circulating pumps, or by thoroughly impregnating or saturating the goods in souring or chemicing machines, and then letting them stand in heaps for some time. The latter method is simplest and is most widely used in England at the present time, whereas the former possesses the advantage of putting less strain on the goods.

Many firms adopt the following series of operations: (1) Singeing, (2) liming and filling in lime keir, (3) bowking (*i.e.*, boiling in keir), (4) washing and souring, (5) washing and filling in soda keir, (6) bowking, (7) washing and chemicing (*i.e.*, treating with bleaching chemicals), (8) souring, washing, and *squeezing off*.

The process of **Mercerisation** of cotton goods is described on p. 205.

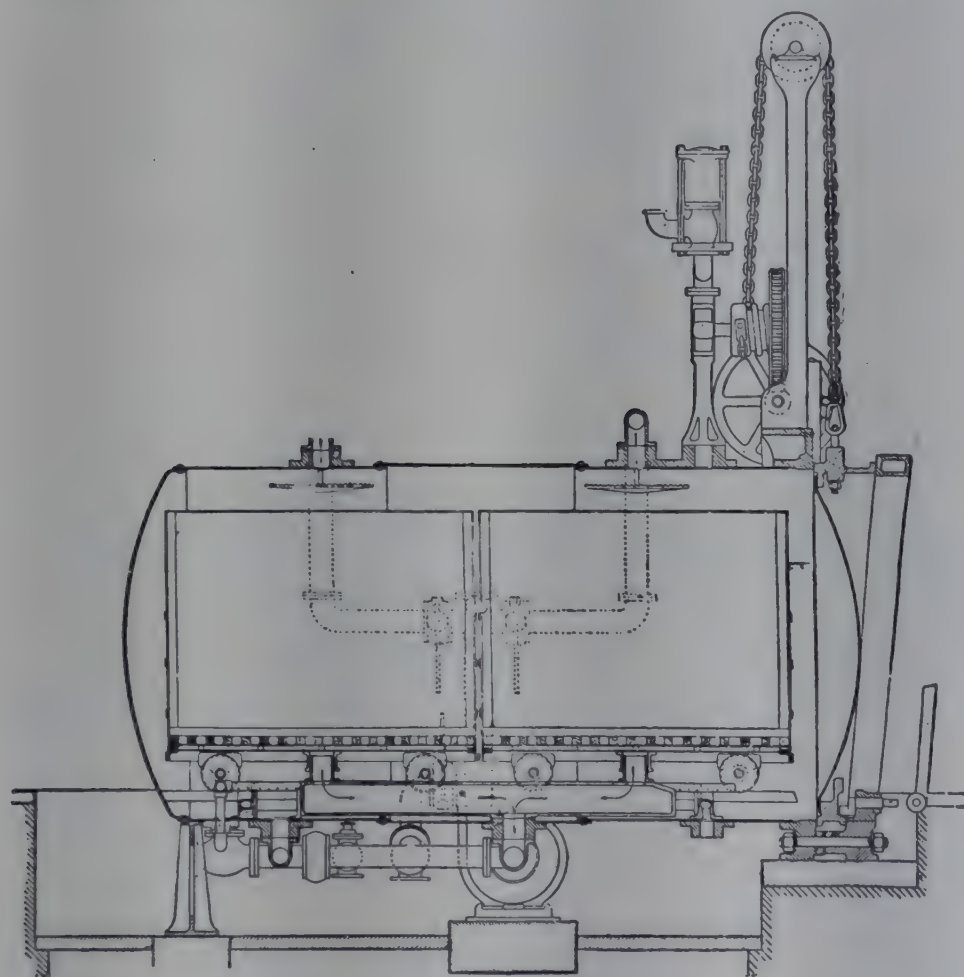


FIG. 203.—Mather Patent Kier (Section).  
(Mather & Platt, Manchester.)

**Bleaching of Wool.**—Before subjecting to the bleaching chemicals all oil (used in spinning the wool) is carefully removed by washing with ammonium carbonate, soda, or soap: soft water must be used for the purpose. The wool is then bleached either by treating with a bisulphite solution or by exposing it moist to the fumes ( $\text{SO}_2$ ) of burning sulphur. For the latter purpose sulphur—about 8 per cent. of the weight of the wool to be treated—is burnt in closed chambers in which the wool is suspended.

A very good white is obtained by bleaching with **Hydrogen peroxide**,  $\text{H}_2\text{O}_2$ ; a dilute solution is made weakly alkaline with ammonia and the wool immersed until white. (Hydrogen peroxide is also used for bleaching silk, ivory, hair, etc.). **Sodium peroxide**,  $\text{Na}_2\text{O}_2$ , has also been used. This thrown into water decomposes, yielding oxygen and caustic soda. The oxygen bleaches the wool, although much available oxygen escapes unutilised in the free state. Since the caustic soda produced

attacks the wool, magnesium sulphate (Glauber's salt) is added to destroy its corrosive effect. The sodium peroxide process is neither so easy nor certain as the hydrogen peroxide or sulphite process.

Sometimes before the wool is finally passed on to the dyer and printer it is

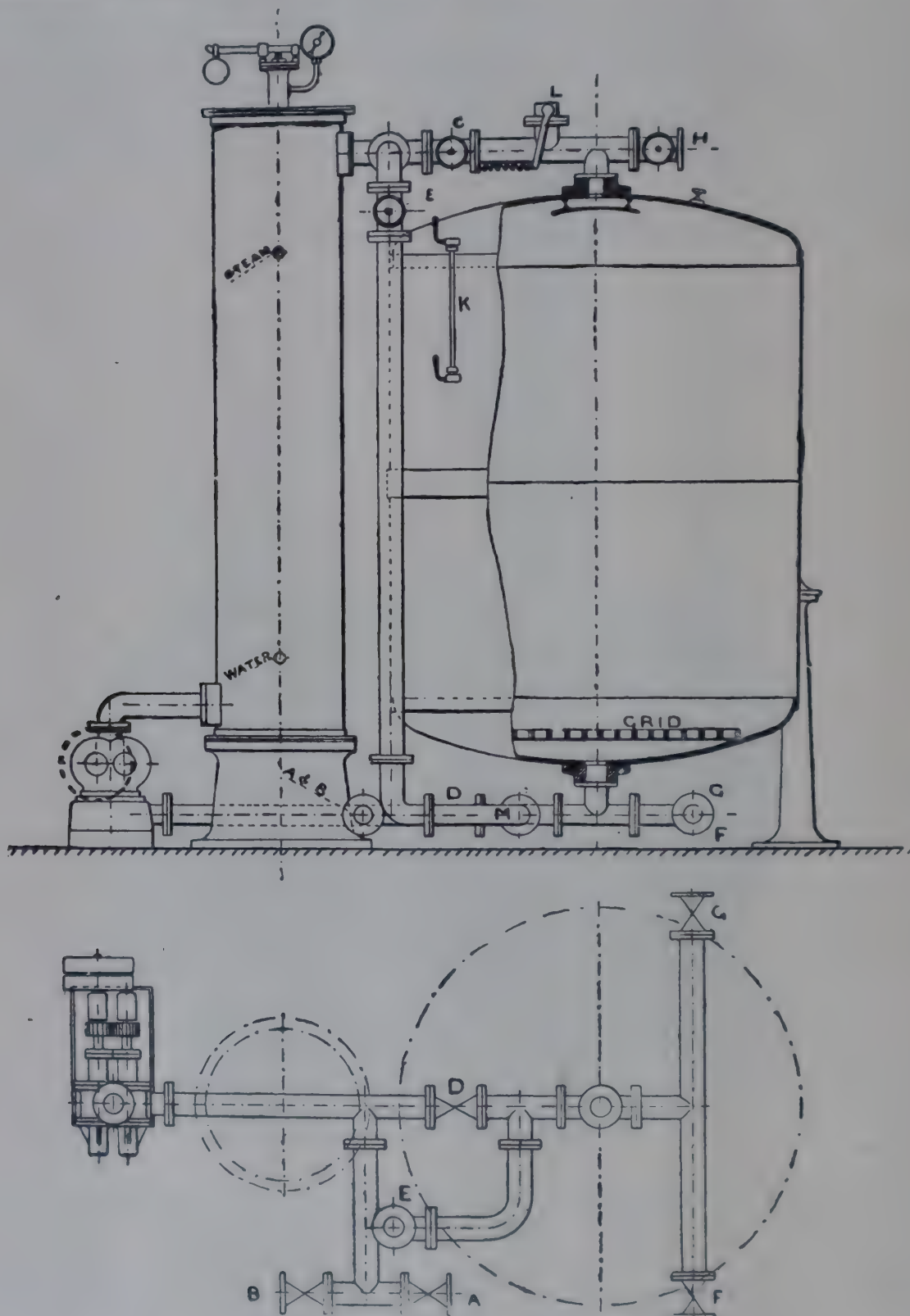


FIG. 204.—Farmer's High Pressure Kier, with Multitubular Heater and Pump.  
(Sir James Farmer & Sons Ltd., Manchester.)

subjected to a very weak bleaching powder solution, mordanted with sodium stannate ("Tin salt"), and then treated with dilute sulphuric acid. Wool treated thus dyes very well.

**Silk Bleaching.**—After "degumming" (see **Silk**, p. 517) by warming with



neutral soap solution and then (if the silk has to be dyed a light shade) by "white boiling" (see p. 518), the silk may be directly transferred to the dye bath; the "boiled-off baths" containing the silk gum dissolved in the soap solution used for degumming are used in the dye baths. Occasionally silk is bleached with hydrogen peroxide or sulphur dioxide, and, indeed, **wild silks** must be bleached with hydrogen peroxide. Modern silks are strongly "weighted" with tin chloride, water-glass, and sodium phosphate, the weight being sometimes doubled thereby without injury to the lustre or dyeing power of the silk. However, such weighted silk is far less strong and durable than the pure silk; indeed it is scarcely better in these respects than artificial silk. When the silk is to be dyed a dark shade, such weighting and colouring agents as tannic acid and potassium ferrocyanide, iron sulphate, etc., may be used.

**Linen Bleaching.**—This may be carried out by spreading the material on meadows in bright sunshine, keeping the material well sprinkled with water. The sunlight causes the formation of hydrogen peroxide, or ozone, which oxidises the lignin. As a result the linen acquires the snow-white colour so characteristic of it. This process is effective with the **very finest yarns**, given ample time. But the bleaching of the finest yarns is accelerated and improved by one or two boilings in an alkaline bath during the process.

**Bleaching of Heavy Yarns.**—The treatment of the **heavier yarns**, and especially the yarn spun from the shorter fibres (known as "**tow**" yarn), is almost entirely a chemical one, and for "high" colours long and complicated. The flax fibres which are spun into the coarser counts consist of cellulose fibres, together with much extraneous matter, such as woody fibre, decayed cell, and colouring matter. There is also present resinous, waxy, and oily matter which act as a sort of natural varnish, and protect the conglomerate fibre from chemical and atmospheric influence. At the same time they are liable to decay, and so encourage certain ferments and mildews. The first process is to dissolve these by boiling in an alkaline solution. The next process is to attack the unwanted matter by the oxidising effects of a bleaching solution. A treatment with sulphuric acid follows. The way in which the acid acts is obscure, but it tends to destroy the woody matter, and probably has a chemical action on the cellulose. Many practical men, however, suppose it simply "kills" the bleach. A washing in water follows, and the process is repeated again *de novo* until the correct colour is obtained. In order to obtain a full white, a linen yarn may have to undergo the following twenty processes:—

1. Boil in alkaline solution.
2. "Reel" in bleaching solution.
3. Sour with sulphuric acid.
4. Wash in running water.
5. Boil in alkaline solution.
6. Reel in bleach.
7. Sour in sulphuric acid.
8. Wash in running water.
9. Boil in alkali solution.
10. Expose to atmosphere on grass for seven days, turning after four days' exposure.
11. Immerse in steep amongst bleaching solution for twelve hours.
12. Sour with acid.
13. Wash in running water.
14. Boil in alkali solution.
15. Expose to weather as in 10.
16. Immerse in bleaching solution.
17. Wash in running water (often this wash can be left out).
18. Sour in acid bath containing "shading" colour blue or violet).
19. Wash thoroughly.
20. Finish in soap bath (usually with mixed soaps, often with a considerable amount of ammonia soap).

It takes four weeks to make a full white on linen yarn. The treatment is often stopped at fourteen, the boil being replaced by soap finish. This is known as three-quarter white, and is the most common bleach colour.

From the above it will be seen that the object of the bleacher is to remove the extraneous matter without damaging the cellulose fibre. In doing this thoroughly, as much as 50 per cent. of the weight of an average "tow" yarn may be removed. The machinery required for linen bleaching is extensive and well developed, and the chemical treatment is the result of experience.



## Some Modern Literature concerning Bleaching

*Bleaching Methods and their Present-day Significance.*—W. Hundt (*Textil-Praxis*, 1948, **3**, 51–53). Formulae for bleaching cotton, rayon, and their mixtures by  $\text{Cl}_2$ , peroxide, or combined processes are detailed.

*Laundry Bleaches.*—M. A. Lesser (*Soap*, 1948, **24**, No. 11, 37–40, 143, 145). The functions, applications, and control of oxidation bleaching agents, particularly sodium and calcium hypochlorites, peroxides, and perborates. There is an extensive bibliography.

*Bleaching Process and Composition.*—Dockport Cotton Batting Co. B.P. 591, 537, 18.7.44) Cellulosic fibres are treated in the cold with a halogen-containing bleaching agent, such as a hypochlorite in the presence of an inorganic  $\beta$ -glucosate, such as sodium tetraphosphoglucosate, which is soluble in hot water and is precipitated in colloidal form by bivalent ions to form particles around mineral matter, which in the presence of the glucosate would form an incrustation on the fibres.

*Evaluation and Comparison of Two Commercial Bleaching Processes.*—J. H. Kettering and R. M. Kraemer (*Amer. Dyestuff Rep.*, 1946, **35**, 285–287). The two processes are the single boil hypochlorite and the double boil hydrogen peroxide bleach.

*Bleaching Textiles with Peroxides.*—R. Mills (*Amer. Dyestuff Rep.*, 1946, **35**, 388, 393). Continuous bleaching process for woollen goods and cotton goods by means of hydrogen peroxide.

*Application of Fluorescent Blueing Agents.*—L. Bonnet (*Jour. Text. Instit.*, 1948, **39**, 32; *L'Industrie Textile*, 1947, **64**, 154–155). Geigy's Tintopal, I.G.'s Blankophors, and Lever's coumarin, stilbene, and benzidine derivatives are described.

*Application and Mode of Action of Bleaching Compounds.*—E. Kayser (*Text. Praxis*, 1948, **3**, 281–282). Hydrogen peroxide, sodium peroxide, sodium perborate, sodium percarbonate, and potassium permanganate are described.

*Activation of Peroxide Solutions by Hæmoglobin.*—W. Kind (*Meliand Textilber.*, 1947, **28**, 269). Alkaline peroxide baths cannot be used for bleaching bloodstained cotton because of the decomposing action of hæmoglobin on peroxides.

*Hydrogen Peroxide—Application in Bleaching.*—V. W. Slater and K. W. Richmond (*Dyer*, 1947, **98**, 658–662; *J. Text. Inst., Manchr.*, 1948, **39**, A294). The properties of hydrogen peroxide in the presence of activators and stabilisers. Application to the bleaching of the more important natural fibres and rayons. Future developments are indicated.

*Application and Mode of Action of Bleaching Compounds.*—E. Kayser (*Text. Praxis*, 1948, **3**, 213–215). The characteristics of chlorine, sodium hypochlorite, hypochloric acid, sodium chlorite, chlorine water, and bleaching powder are described.

*Cotton Fabrics, their Bleaching and its Effect on Strength and other Properties.*—J. H. Kettering and R. M. Kraemer (U.S. Dept. of Agric., Aug. 1947, Tech. Bull. 941; *J. Text. Inst., Manchr.*, 1948, **39**, A294).

*The Bleaching of Jute with Chlorite.*—P. B. Sarkar and H. Chatterjee (*J. Text. Inst. Manchr.*, 1948, **39**, T274–281).

*Optical Bleaches.*—S. Cohen and F. Gruenwald (*Rayon synth. Text.*, 1948, **29**, No. 10, 89–91). Properties of the optical bleaching agents such as those containing diaminostilbene, benzimidazole, diazalone, or benzidine structures are described together with requirements for improved agents.

*The Effect of Bleaching on Resistance to Washing.*—I. Mutti (*Boll. Cotoniera*, 1940, **35**, 121–124). Deals with loss of dry and wet strength after bleaching.



## PART III

WATERPROOFING AND FLAMEPROOFING  
TEXTILE FABRICS

## LITERATURE

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ANDÉS.—“Feuersicher-, Geruchlos-, und Wasserdichtmachen.” Vienna, 1896.

EISENSTEIN.—*Allg. Chem.-Ztg.*, 1905, p. 507.

GEOFFREY MARTIN AND JAMES WOOD.—“Notes on the Quantitative Testing of Rainproof and Waterproof Cloth.” *Journ. Soc. Chem. Ind.*, 1919, 38, 841.

Several distinct methods of rendering fabrics waterproof are practised:—

**Waterproofing with Aluminium Acetate.**—The fabric is impregnated with a dilute solution, 5° Bé., of aluminium acetate (which is often prepared by the waterproofer himself by treating alum or aluminium sulphate with calcium acetate or lead acetate), dried in hot air, and drawn through a 5 per cent. soap solution. Insoluble aluminium soaps are precipitated on the fibre and render the material waterproof:—

Aluminium acetate + Sodium soap  $\longrightarrow$  Aluminium soap + Sodium acetate.

A trace of undecomposed soap remains in the fabric; this, after drying, would give the fabric a soft slippery feel; it is therefore removed by passing the soaped fabric through a solution of alum or aluminium acetate, rinsing and drying.

Impregnating the fabric with aluminium acetate and completely drying at a steam heat will render the fabric fairly waterproof owing to the formation of insoluble aluminium compounds in the fibre. Sometimes this alone is done; sometimes the fabric is, after drying, passed through an alum solution in order to render the fabric more completely waterproof. India-rubber, paraffin, etc., is introduced into the soap solution (soap solutions form emulsions with fused waxes and paraffin, petroleum, rubber solutions, etc.). Japan or Carnaüba wax is often used. The rubber is dissolved in paraffin, linseed oil, and palm oil.

The Badische Anilin- und Soda-Fabrik recommend the two following processes for waterproofing dyed cotton or linen material:—

(1) Soak the dyed pieces in a solution of 5 lbs. soap in 100 gals. water, squeeze, pass through a solution of 10 lbs. alum in 100 gals. water; squeeze and dry. Repeat whole process if necessary.

(2) Prepare a soap emulsion by boiling together 6 lbs. white soap, 3 lbs. tallow, 3 lbs. stearine. Pass the dry pieces through the emulsion at 70°-85° F., squeeze, and pass through a cold solution of aluminium acetate of 5° Tw. Rinse lightly and dry hot.

It should be noticed that by this method the interstices between the threads are not filled up, the fibres keeping the water back mechanically. In true waterproofing this should always be the case.

According to German Patent 141,411, fabrics are waterproofed without destroying their porous nature by impregnating with aluminium acetate, drying, and impregnating with lanoline or wool-fat dissolved in volatile solvent.

**Waterproofing with Paraffin.**—The materials are passed through a dilute solution of paraffin, ceresine, or similar body, dissolved in light petroleum or other volatile solvent. The solution fills the cells of the fabric and the solid matter is left behind when the solvent evaporates.

Sometimes the ceresine, paraffin, etc., is applied in a *melting state* by means of rotating a metallic roller in contact with the solid hydrocarbon, so that it carries away portions of it and puts them on the fabric, which passes between the roller and a heated trough; the latter fuses the hydrocarbons so that they are soaked up by the fabric as fast as they are fused. The goods are finally calendered.



**Waterproofing with Gelatine, Tannin, Caseinate of Lime, Chrome Gelatine.**—The materials are treated with glue or gelatine and afterwards with tannin or alum which renders the gelatine insoluble (see **Gelatine**).

Cotton goods are often treated with 1.5 kg. of gelatine in 50 l. of boiling water containing 1.5 kg. soap chips, 2.5 kg. alum. The cotton is put through the solution at 50° C., dried, and calendered. Cellulose materials are often waterproofed by impregnating with a solution of 1 part gelatine, 1 part glycerol, 1 part tannin in 12 parts water.

Sails, carriage aprons, tarpaulins, etc., are often saturated with gelatine solution (7 per cent.) at 40° C., air dried, passed through a 4 per cent. alum solution, air dried, rinsed, dried. Sometimes the materials are impregnated with chrome gelatine, which is rendered insoluble by exposing the material to light. A well-known recipe consists in dissolving 5 parts gelatine, 1 part potassium bichromate, and 1 part of acetic acid in 30-50 parts of water, adding 5 parts of cuprammonium (ammoniacal solution of copper oxide), brushing the material on the fibre, and drying in air.

Casein waterproofing is carried out by stirring it into a cream with water, and adding 2.5 per cent. its weight of slaked lime; then dissolving casein in alkali solution, mixing the solutions, impregnating the fabric with the mixture, and passing it through aluminium acetate solution, which precipitates an insoluble aluminium caseinate.

**Waterproofing with Cuprammonium, Viscose, and other solvents for cellulose.** The celebrated Willesden fabrics are made this way by cuprammonium. For details see under **Cellulose**, pp. 189, 213.

**Waterproofing with Solutions of Caoutchouc.**—See under **India-rubber**, p. 360.

**Waterproof Oiled Fabrics** are made by spreading over the material in several successive layers a paste consisting of half-raw and half-boiled linseed oil, mixed with mineral colouring matter. The material is dried between the successive applications. Siccatives, resin, petroleum, etc., are sometimes added. For **Oil Cloth** and **Linoleum** see p. 49.

Tarpaulins are made by painting suitable fabrics with tar which has been heated to drive off the more volatile oils (but under 300° C., otherwise the tar becomes unsuitable).

**Manufacture of Non-Inflammable Fabrics.**—Clothes and fabrics may be made almost unflammable by soaking in a solution of alum, ammonium phosphate, borax, water-glass, and similar chemicals. Sodium tungstate has been used for making ball dresses non-inflammable; borax and alum, borax and magnesium sulphate, gypsum and ammonium sulphate are all good mixtures. Water-glass makes the material stiff. Ammonium phosphate leaves the material soft. A full account is given in Andés' book, "*Feuersicher-, Geruchlos- und Wasserdichtmachen*" (above).

W. H. Perkin's method of *permanently fireproofing cotton goods* (e.g., "non-flam." flannelette) is this:—The flannelette is impregnated with a solution of sodium stannate of about 45° Tw., squeezed, dried on heating copper drums, passed through ammonium sulphate solution of 15° Tw. (in order to precipitate tin oxide), squeezed, dried, washed to remove Na<sub>2</sub>SO<sub>4</sub>, dried and finished in the usual manner. The treated material can be dyed the most delicate shades, has no poisonous action on the skin, and is stronger and more durable than the untreated material. The cost is not more than 1d. per yard with tin at £210 per ton. Muslin curtains can be treated similarly (see W. H. Perkin, *Eighth Int. Cong. Appl. Chem.*, New York, 1912). Also Patents—French Patent, 321,063 of 1902; English Patents, 8,509, 1902; 24,222, 1903.

**Flameproofing Textile Fabrics.**—A. C. Nuessle (*J. Soc. Dy. Col.*, Bradford, 1948, 64, 342). Structure of the complex formed when urea and phosphoric acid are dried into cellulosic fabric.

For modern statistics see Appendix III.

**Analysis of Waterproof Fabrics.**—The methods are fully discussed by Geoffrey Martin and James Wood in the *Journ. Soc. Chem. Ind.*, 1919, 38, 841, which see.

Absolute waterproof articles are uncomfortable to wear because they are not permeable to air. Hence most of the so-called "waterproofs" are intended to admit air, and are permeable to water after some time.

**Drop Test.**—Water is dropped from a burette at the rate of 20 drops per minute upon the cloth placed 5 ft. below. The cloth is placed on a sheet of white blotting paper, which in turn is placed on a sheet of plate glass, placed at an angle of 45° C. above a glass mirror. After a time the drops of water pass through the cloth, and wet the blotting paper. The dark stain of moisture is immediately seen in the mirror below the glass plate.

The British War Office require a cloth to stand 60 drops.

For civilian use a cloth which stands 10-18 drops is good enough.

**Determination of Ash.**—A weighed sample is ignited in a porcelain dish.

**Determination of Matter Soluble in 3 per cent. Hydrochloric Acid.**—The fabric is treated with the acid for fifteen minutes.



*Determination of Ether Extract* is carried out in a Soxhlet apparatus.

The *weight of the fabric* in ounces per yard is determined by weighing 1 sq. ft.

The *tensile strength* of the material should be determined.

The *amount of wool, cotton, and silk present* is determined as follows:—The wool is separated from the cotton by boiling with 5 per cent. caustic potash solution for fifteen minutes; 4 per cent. is then added to the weight of the cotton residue. The difference between this figure and 100 per cent. represents the amount of wool present.

Wool can be separated from silk by immersing the fabric in concentrated hydrochloric acid for three minutes at 50° C., when the silk dissolves.

Linen is separated from silk by treating with an alkaline glycerol-copper solution, wherein the silk dissolves.

**Fabrics Proofed with Rubber.**—In the case of fabrics proofed with india-rubber the War Office has distinct specifications as regards the composition of the proofing material.

Thus the material for proofing coats with vulcanised india-rubber mixings must contain: *mineral matter*, not more than 41 per cent.; *sulphur*, not more than 3 per cent.; *india-rubber*, not less than 56 per cent. on the average, and no single coat may contain less than 54 per cent. In the case of cyclists' waterproof capes, however, a different composition may be used for the proofing. The *mineral matter* must not exceed 52 per cent.; *sulphur*, 3 per cent. (the free sulphur in this to be not more than 1 per cent.). The india-rubber must not be less than 45 per cent. on the average, and no single garment may contain less than 43 per cent. Civilian garments may consist of different qualities from these, which represent a very high class of waterproofing.

**Mineral Matter.**—A part of the sample is ignited and the weight of the ash determined. Due corrections are made for oxidation to sulphates. When antimony, sulphide, and copper are present these should be estimated in the usual way. The mineral matter used for colouring the proofing of cyclists' capes usually consists of zinc oxide and litharge. Small additions of other ingredients as are generally recognised as having a beneficial influence are officially recognised.

The presence of calcium carbonate and magnesium carbonate is often prohibited in War Office contracts.

**Sulphur** is estimated in the usual way as barium sulphate, oxidation being generally effected by nitric acid and potassium chlorate. From a determination of the amount of antimony and other metals present as sulphide in the preliminary operation, a correction for the amount of sulphur combined with antimony and other metals can be made.

**Free sulphur** is the sulphur extractable by boiling acetone. The substance is extracted with boiling acetone for one hour, the acetone evaporated, the residue oxidised, and the amount of "free" sulphur determined as barium sulphate.

The **organic matter** extracted by acetone is the difference between the total acetone extract and free sulphur.

**Alcoholic Potash Extract.**—The amount of organic matter dissolved by boiling the acetone-extracted sample with alcoholic potash is estimated as follows: The acetone-extracted rubber is dried and boiled for eight hours with a solution of alcoholic potash (56 g. KOH in 500 c.c. alcohol). The solution is poured into a dish, the rubber washed twice with alcohol, and boiled two or three times with water, the washings added, and the alcohol distilled off and recovered. The residue is evaporated, washed into a separating funnel, acidified with hydrochloric acid, and the fatty acids extracted with successive portions of ether. The ether is distilled off and the residue dried to constant weight in the water oven.

The rubber residue left after boiling with alcoholic potash is washed free from potash by water, dried to constant weight in the water oven, and cooled *in vacuo*. The ash and the sulphur in the dried residue are then estimated, and hence the weight of organic matter in the residue is calculated. This weight is deducted from the weight of organic matter in the residue after extraction with acetone (obtained by deduction of ash and combined sulphur), and from the difference the loss of organic matter by extraction with alcoholic potash per 100 parts of rubber is calculated.

The india-rubber proofing should be free from grit and large sized particles. In the case of capes a 3-in. square of material should have at least 0.13 g. of proofing between the two fabrics.





## SECTION XVIII

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### Dyeing and Colour Printing Industry





# DYEING AND COLOUR PRINTING INDUSTRY

Originally written by HENRY J. S. SAND, D.Sc., Ph.D.  
Revised by E. I. COOKE, M.A.(Cantab.), B.Sc., A.R.I.C.

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## INTRODUCTION

THE object of the dyer of textiles may be said to be to impart to them, by treatment with certain solutions, a uniform colour which should be as permanent as possible to solvents and other influences. The methods of obtaining this end are manifold, and it is not to be supposed that any one explanation will fully cover all the processes employed. Even where the operations carried out in various cases are apparently similar or identical, the theory underlying them may be entirely different.

The simplest classification of dyestuffs is that, into those which are taken out of solution directly by the fibre, and into those which are produced chemically as insoluble substances during successive operations of dyeing. The former are usually termed “**substantive**,” the latter “**adjective**” dyes. Dyestuffs like indigo which are reproduced in the fibre in their original condition, during successive operations, are usually said to belong to the former class, although, according to the definition just given, they would more correctly be considered to be members of the latter. Another classification often employed is that into “direct” dyes, *i.e.*, practically the same as substantive dyes and “**mordant**” dyes, *i.e.*, such as can only be applied with the intervention of a mordant. Lastly, dyes are sometimes spoken of as “**monogenetic**” when they will yield only one colour whether applied directly or with the aid of different mordants, and as “**polygenetic**” when they will yield different colours according to the mordant employed.

**Substantive or Direct Dyes.**—If a piece of silk, wool, and cotton be each boiled with the solution of a basic dye, such as Victoria blue or the acidified solution of an acid dye, such as acid magenta, it will be found that the silk and the wool have been dyed, whereas the cotton will probably only have acquired a slight stain which may be easily removed by washing. If the solution of the dyestuff be fairly dilute the animal fibre will remove all of it, leaving a colourless liquid behind. Again, when wool or silk is dyed with the hydrochloride of a basic dye, such as magenta (rosaniline hydrochloride), it has been shown by Knecht and Appleyard



that the whole of the hydrochloric acid is left in solution and the fibre is dyed red, in spite of the fact that the base which alone has been removed from solution is colourless. Indeed it was shown by Jacquemin as early as 1876 that when either wool or silk is boiled with a colourless solution of rosaniline base, it is dyed red. These facts all point to the conclusion that the dyeing of animal fibres with most of the basic dyes is a process of a more or less chemical nature, consisting of the combination of some substance contained in the fibre with the base of the dye. Experiments may also be adduced to show that the dyeing of animal fibres with the majority of acid dyestuffs is a similar process, a conclusion which need not surprise us, for we have every reason to believe that not only wool and silk, but also most of the substances which may be formed from them by chemical decomposition, are of the nature of amido acids, *i.e.*, they have the properties both of acids and bases, and will, therefore, readily combine with dyestuffs having basic or acid properties.

The following facts may further be adduced to confirm the conclusion that acid and basic dyestuffs are usually held by the animal fibres in a very firm manner approaching that of chemical combination. It has been shown by Dreaper in numerous cases that, when held by the animal fibre, a dyestuff is much less readily acted upon chemically than when it is in combination with a vegetable fibre, such as cotton, or than when it is in the free state. Thus, the direct cotton dye primuline was dyed on samples of silk and cotton and then diazotised. In the former case the resulting compound was shown to be incapable of coupling with R salt, whereas in the latter combination instantly took place just as if the diazotised dye had been in the free state. Similarly, the acid dye methyl orange is not turned red so readily by acid when on silk as when in solution, which points to the conclusion that it forms an orange compound with the silk. Then again, it has been shown by Knecht that the laws which govern chemical combination are to some extent obeyed; for when different acid colouring matters of similar composition were employed in the dyeing of wool in strong solution and under similar conditions, the quantities taken up by the fibre stood in the ratio of their molecular weights.

The action on the fibre during the process of dyeing of substances other than the dyestuff is probably of the very greatest importance. Thus it appears that two slightly soluble substances which have been named respectively lanuginic and sericinic acid are produced by the action of hot water or acid on wool or silk, and it is these substances which combine with the basic or acid colouring matters of the bath. In fact it has been shown by Knecht that if wool is first boiled with 5-10 per cent. sulphuric acid, and then thoroughly washed, it dyes fuller shades in the neutral bath of acid colours than would be obtained in the ordinary way even if acid were added. This experiment is of great interest, for it shows that what is actually dyed by chemical combination is probably not the whole of the fibre, but mainly a constituent produced from it by the action of water during the operation of dyeing. Furthermore it opens up the probability that the chemical process takes place largely in solution, a chemical compound of lanuginic or sericinic acid with the dye being first produced in the liquid, and then absorbed by the fibre by one of the processes of solid solution or colloidal precipitation discussed in the sequence. The fact that many dyes may be extracted from wool and silk by alcohol is sometimes adduced as an argument against chemical combination, but what is extracted in this case may very possibly usually be the chemical compound of the dyestuff with lanuginic or sericinic acid, and not the dyestuff itself.

The dyeing of cotton is probably under all circumstances a process of a slightly different order from that usually taking place with the animal fibres. During the last twenty-five years a large number of direct cotton dyes has become known. When cotton is treated with the solution of any one of these substances, it will extract a considerable amount of dyestuff from solution, and thus become dyed; the remaining liquid will, however, be found to be by no means colourless but to retain a very large proportion of the dyestuff. Again, if the dyed fibre be treated with pure water a considerable proportion of the dye will be extracted, and by repeating the operation almost the whole may be withdrawn. The process of dyeing in this case is thus seen to be a "reversible" one, and may fairly be compared with what takes place when the solution of a substance soluble in water such as benzoic acid is shaken with a liquid such as ether in which it is likewise soluble. The solution in ether



which is thus obtained may be compared with the dyed fibres; and the latter may be termed a "solid solution" of dyestuff in the cotton.

The introduction of the idea of solid solution into the theory of dyeing is due to O. N. Witt, who, however, attempted primarily to apply it to animal fibres. A law which particularly characterises solution in contrast to chemical combination is that known as Nernst's distribution law. In its application to the dyeing of fibres this law demands that if a series of experiments is carried out in which given weights of the same fibre are dyed in a given volume of the solution of the same dyestuff, containing, however, different quantities of the latter in each experiment, then after equilibrium has been established, the expression  $C_f : C_s \frac{1}{n}$  should have the same value in each experiment. In this expression  $C_f$  indicates the amount of dyestuff taken up by the fibre,  $C_s$  the amount left in the solution, and  $n$  the ratio of the molecular weight of the dyestuff in solution and on the fibre respectively. It has been shown particularly by v. Georgievics that this relation does hold for the dyeing of cotton in many cases, and also in a few for the dyeing of wool and silk. It must be pointed out here, however, that a relation of similar form holds for the process of "adsorption" of colloids discussed in the sequence, and that experiments on distribution like those of v. Georgievics can, therefore, not distinguish between the phenomena of solution and adsorption.

**Adjective Dyes.**—In all cases where the dyestuff is produced as an insoluble substance by the interaction of two soluble ones in the interior of the fibre, the processes of chemical combination with the fibre and solid solution in it may play a part, but in addition we have the possibility of the solid being trapped by the cell walls in a purely mechanical manner, and also that it may be held by them by the phenomenon of adhesion. It must be pointed out here that there are no doubt continual gradations possible between purely mechanical processes, the physical phenomena of adhesion, adsorption, and solid solution, and finally the process of chemical combination; and very probably all these gradations occur in one or another of the manifold operations which are carried out in dyeing.

A physical phenomenon which no doubt plays an important part in many of the processes of dyeing is the formation of so-called "adsorption" compounds. This phenomenon, the importance of which in dyeing has been pointed out in particular by P. Zacharias, has recently led to a "colloid-compound" or "electrical" theory of dyeing.

A large number of substances of importance to the dyer, such as tannin, many dyestuffs, such as congo red, crystal violet (base), night blue base, etc., and the fibres themselves belong to the class of colloids. Many of these substances will dissolve in water, forming what are termed colloidal solutions, *i.e.*, solutions in which the dissolved particles are of a much larger order of magnitude than those of ordinary solutions, so that they will not diffuse through parchment and may usually be made visible by means of the ultramicroscope. These dissolved particles have been proved to bear electric charges, those of a basic nature acquiring a positive, those of an acid or neutral nature usually taking up a negative charge. It has also recently been shown by Gee and Harrison that all the fibres become negatively charged in contact with pure water, whereas in contact with acids they usually assume a positive charge. Now, if a colloidal solution containing positively charged particles is added to one in which negatively charged particles are present, these mutually attract each other and combine, to form what are called adsorption compounds. The latter are precipitated from solution, the electrical charges being neutralised at the same time. There can be little doubt that the "triple" compounds formed between tannin, metal oxides, and dyestuffs, on which the dyeing of basic dyes on cotton mainly depends, are largely due to colloidal combination, and this same phenomenon may probably play an important part in many other processes such as the fixation of metal oxides and other substances on the fibre.

## Water

Most natural waters show an alkaline reaction, and for purposes of mordanting, dyeing with basic colours, and washing after dyeing should be carefully neutralised before use by a suitable acid. Sulphuric or acetic acid may be employed. The latter, though more expensive, is preferable, since a small excess accidentally added will usually not be harmful. When employing the former it may often be advantageous to add a small amount of sodium acetate in order to neutralise the free mineral acid.

For dyeing with acid colours, it will usually be indifferent whether the water employed is originally alkaline or not, since enough acid is always added during the process of dyeing to make the bath strongly acid. For dyeing with direct cotton dyes and sulphur colours hard waters should be softened before use.



Water containing even small quantities of iron or other heavy metals is as a rule useless for dyeing and mordanting operations, since the iron will usually combine with the dye, thus acting as a mordant, and produce a dull or "saddened" colour. The iron must, therefore, be got rid of by a process of softening. For use with acid dyes a very small amount of heavy metals will as a rule not be harmful. The presence of lime in large quantity in a water must be taken into consideration, since it will act as a mordant, and may often produce undesirable results. In some cases, such as in the dyeing of turkey red, the presence of lime is desirable, since it acts as an additional mordant, and produces better shades than would be otherwise obtained.

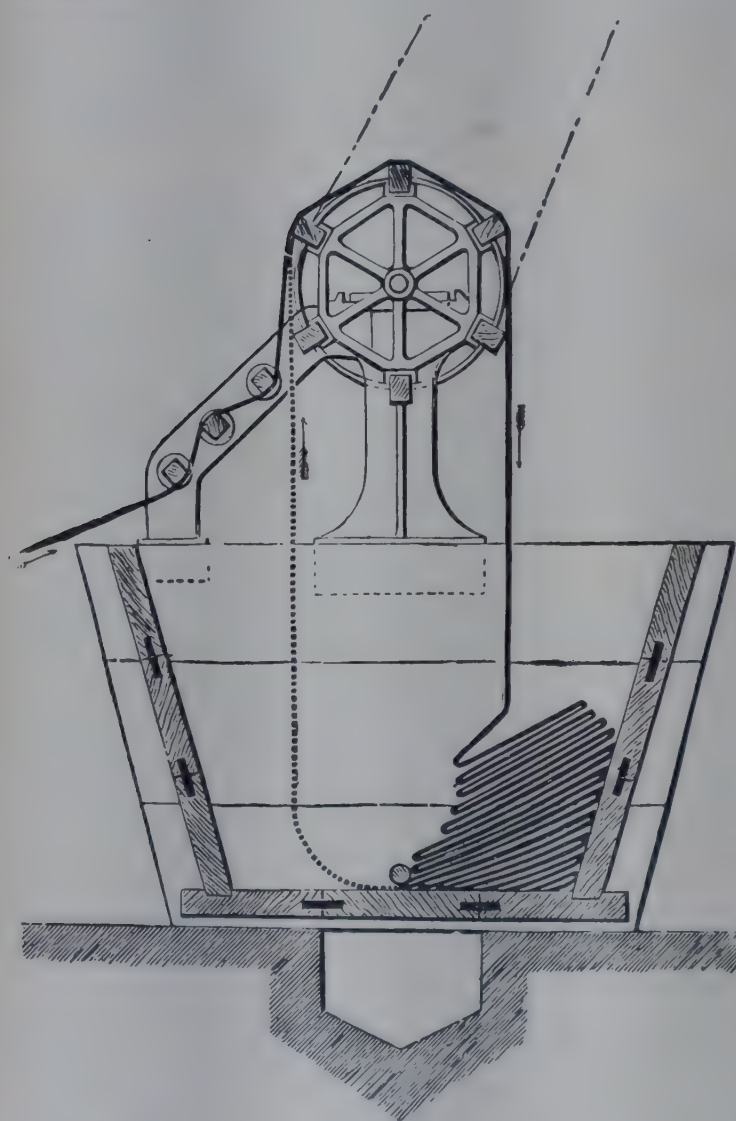


FIG. 205.—Dye Vat and Winch for Pile Fabrics.  
(Mather & Platt, Manchester.)

### Appliances and Machinery used in Dyeing

#### Preparation for Dyeing.

—The material must be freed completely from all fatty impurities by the processes described in the chapters on bleaching before it comes into the dye bath, and this refers not only to such fats and waxes as are naturally present in the fibre, but also to those which are added artificially during the operations of spinning and weaving. Bleaching is usually only necessary when delicate or bright shades are to be dyed. Wool may be carbonised either before or after dyeing in order to remove vegetable impurities such as burrs, pieces of straw, etc. In almost all cases the fibre should be thoroughly wetted out before it comes in contact with the dyeing liquid.

#### Dissolving the Colours.

—All dyestuffs and pastes should be dissolved in condensed water and preferably filtered through cotton cloth before they are added to the dye bath. Dyewoods may be

extracted in the dye vats at boiling temperature before entering the goods. For this purpose the chips are placed in bags and preferably extracted systematically, *i.e.*, the fresh chips should be employed to bring the bath completely up to strength, whereas the almost exhausted wood should be completely extracted in a bath containing fresh water. Special extractors, apart from the dye vats, are also frequently employed, and devices are also in use which may be fitted to the dye baths and in which the wood may be continuously extracted while the latter are in use.

All dyeing machinery may be said to consist of an arrangement for either moving the goods through the more or less stationary dye liquor, or for causing the dye liquor to circulate through the stationary goods. In addition, an arrangement for heating the dye vat, usually either by steam pipes or by live steam, is provided. At the present day the textile fibres are dyed in practically all stages of manufacture; the



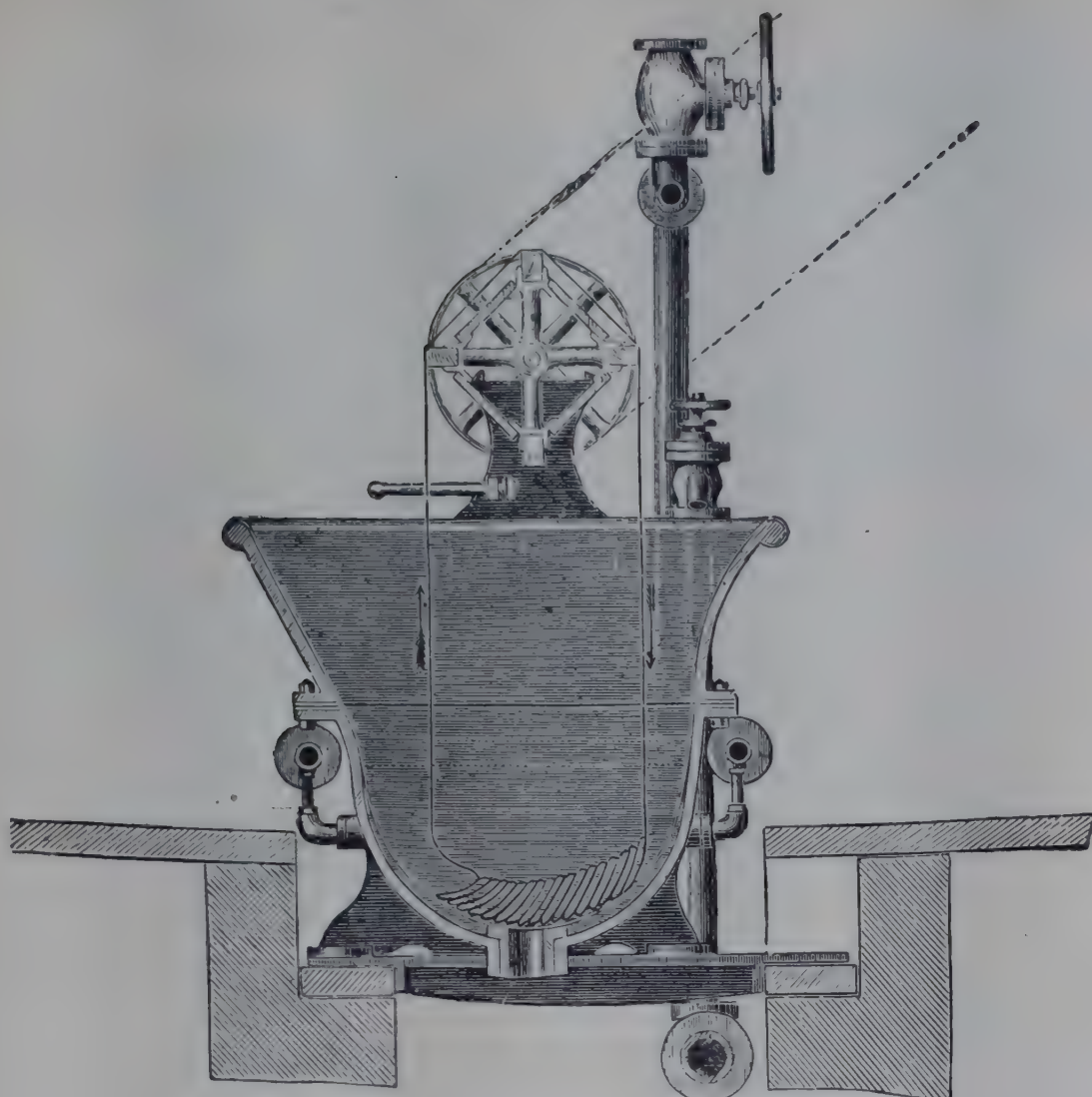


FIG. 206.—Double-Walled Copper Dye Vat.  
(Mather & Platt, Manchester.)

dyeing of the finished cloth, or piece-dyeing, however, still transcends in importance that of the other partially finished forms.

**Dyeing of Piece-goods.**—The simplest form of machine and the one most usually employed for woollen cloth consists of the dye vat and winch.

Fig. 205 shows an arrangement of this kind in which a wooden dye vat is employed. The pieces are stitched together before dyeing and are usually run as an endless band over the winch. The

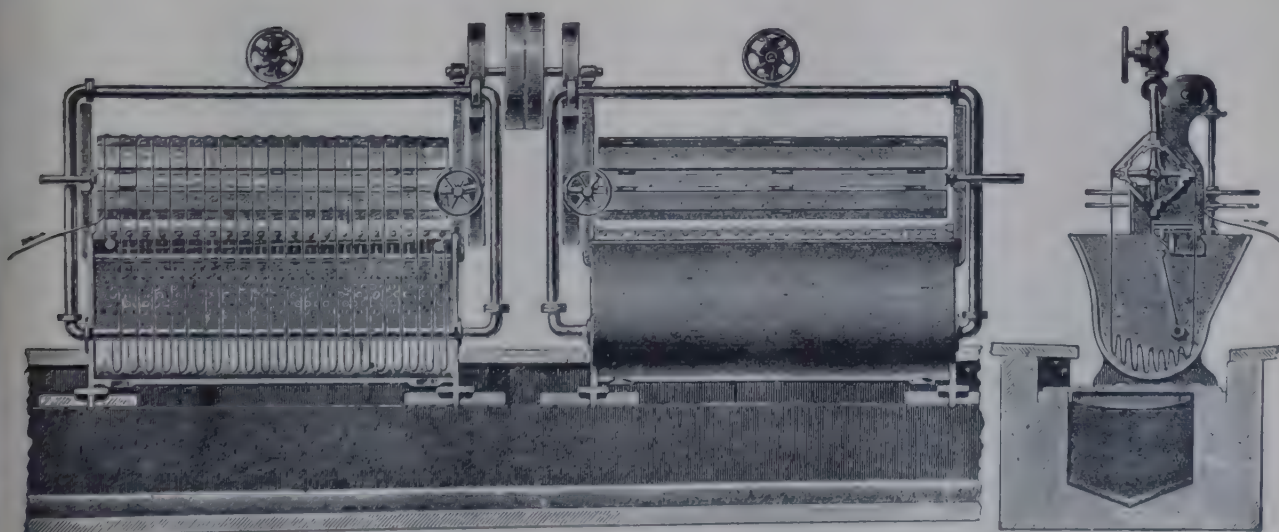


FIG. 207.—Dye Vat. (Mather & Platt, Manchester.)



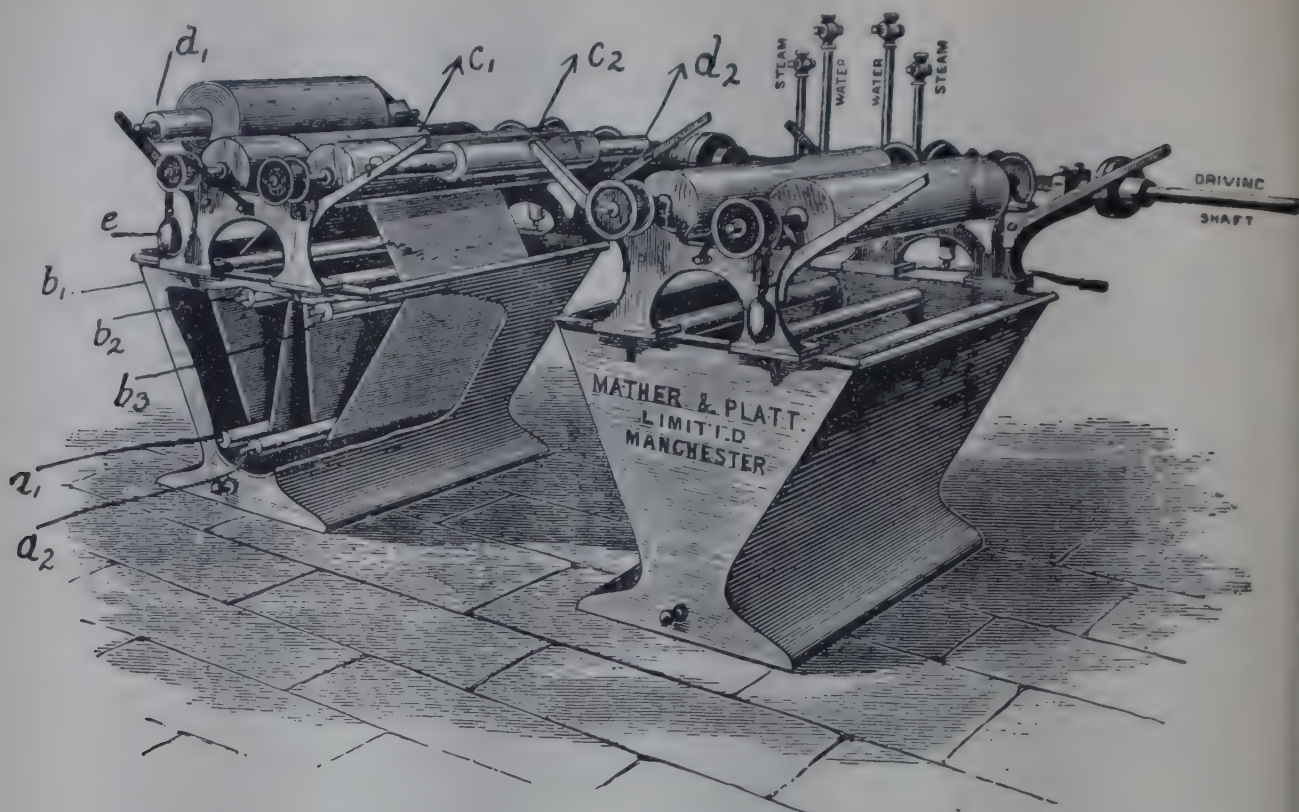


FIG. 208.

FIG. 208a.

Dyeing Jiggers. (Mather & Platt, Manchester.)

latter may be turned by machinery or by hand. The dye bath is usually heated by direct steam issuing from a perforated pipe. Fig. 206 shows a double-walled copper vat which is heated by steam introduced between the two copper walls. In this vat the steam does not mix with the dye liquor, and dilution of the latter is thus avoided during dyeing. Fig. 207 illustrates a vat in which the pieces in rope form are drawn as an endless band in a spiral over the same winch a large number of times after remaining in the liquid for a short time. Guide pegs prevent them from becoming entangled.

The machine most frequently met with in the dyeing of cotton cloth is the jigger. In this machine the cloth in full width is passed through the dye liquor several times over guide rollers.

In Fig. 208 two of these rollers,  $a_1$ ,  $a_2$ , are shown submerged in the liquid, and three,  $b_1$ ,  $b_2$ ,  $b_3$ , are placed above. In addition, two draw rollers,  $c_1$ ,  $c_2$ , and two batch rollers,  $d_1$  and  $d_2$ , are visible above the vat. The cloth is first run from  $c_1$  to  $c_2$ , the roller  $c_2$  being actuated directly by the driving machinery, while the brake  $e$  is placed on  $c_1$ . The cloth is thus kept in a state of tension. When all the cloth has been run on to  $c_2$ , the motion is reversed,  $c_1$  being made the driving roller, and the brake being put on  $c_2$ . This alternate motion is continued until the piece has been dyed the desired

shade. The pipes necessary for the supply of water and steam for heating are indicated in Fig. 12a.

For indigo dyeing, pp. 461 and 554, vats are employed in which the cloth is run over a large series of rollers completely submerged in the liquor. It then passes through squeezing rollers, and over a series of rollers placed in the air above the vat for the purpose of oxidising the leuco compound absorbed by the fibre. Another arrangement shown in Fig. 209 for the purpose of oxidising the leuco compound, consists in piling the cloth loosely on an endless travelling band. The dye vat must be supplied with a stirring arrangement  $G$ , which can be actuated at will when the vat is being freshened up. Several vats of increasing strength are usually

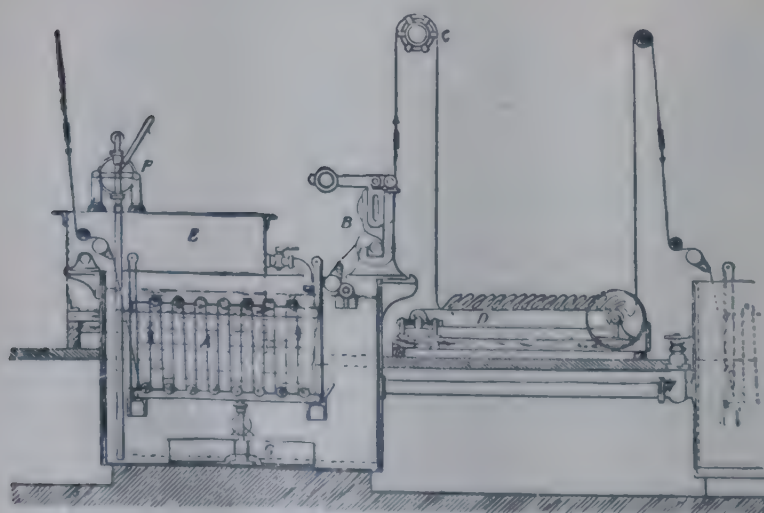


FIG. 209.—Indigo Dyeing Machine.  
(Mather & Platt, Manchester.)



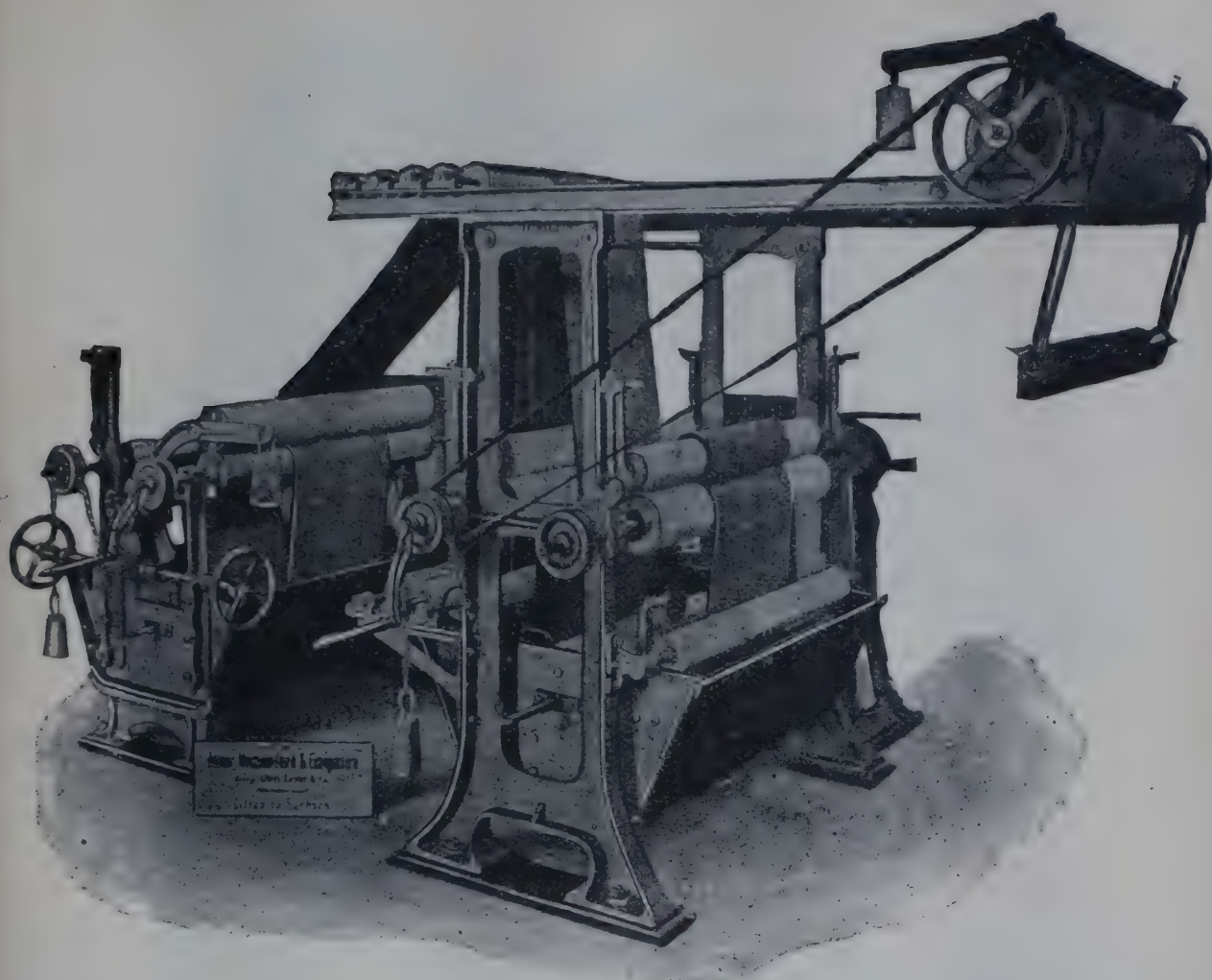


FIG. 210.—Jiggers for Sulphur Blue. (Zittauer Maschinenfabrik.)

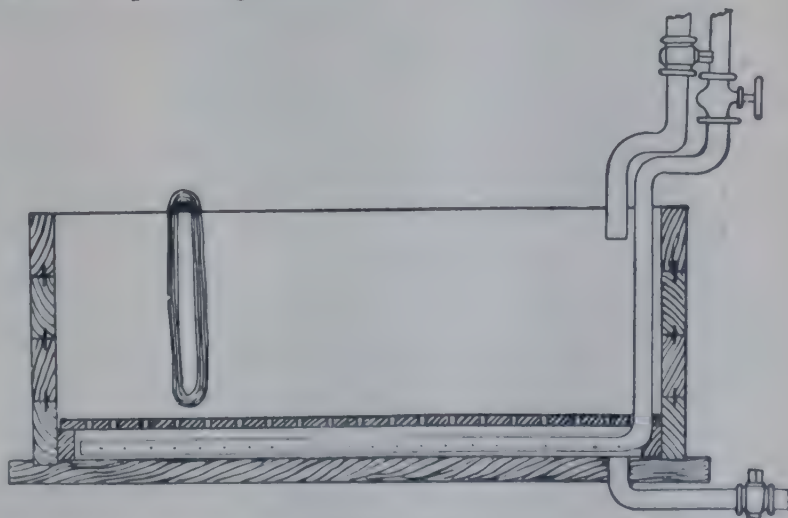
employed in series. For indigo dyeing “dipping vats” are also frequently employed in which the cloth is mounted on frames that are lowered into the dye liquor, after which it is exposed to the air for oxidation.

Fig. 210 shows an arrangement of two jiggers for use in the dyeing of sulphur blue. The first is intended for dyeing, the second for washing the cloth, and an air passage for oxidising the dye is provided between the two jigs (see p. 545). These jiggers are provided with squeezing rollers.

**Padding Machines, *i.e.*,** machines for passing piece-goods through a concentrated solution, differ in principle from jiggers in having much smaller dye vessels or troughs. They are provided with squeezing rollers.

Machines similar in construction to the washing machine shown in Fig. 219 may also be employed in the dyeing of cloth, and like principles may also be adopted in the design of machines for the dyeing of warps.

**Yarn Dyeing.**—Yarn is usually dyed by hand in the hank. For this purpose a rectangular vat, Fig. 211, is employed. It is fitted with the necessary pipes for filling and emptying, and a steam coil, usually perforated, is provided for heating. A false



VAT FOR HANK-DYEING

FIG. 211.



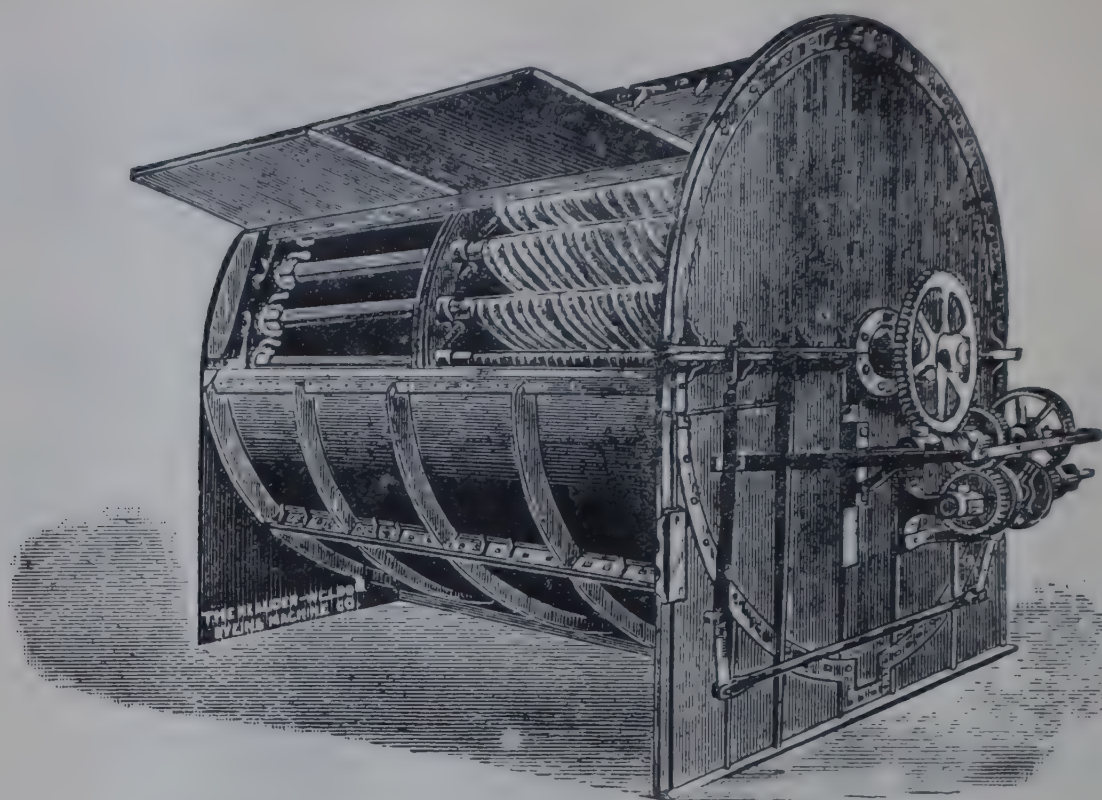


FIG. 212.—Hank Dyeing Machine for Sulphur Colours.  
(Klauder-Weldon Dyeing Machine Co.)

bottom prevents the hanks from coming in contact with the latter. The hanks are suspended on square wooden rods placed across the vat, on each side of which stands a workman. One by one the rods full of yarn are taken up, and to each hank is given a quarter turn, so that the exposed part becomes submerged. This is carried out by means of a thinner rod which is inserted in the loop of the hanks immediately beneath the suspending rod. The rods are arranged in such a manner that there is always a sufficient space of about a foot available beside the rodful of hanks which is being turned.

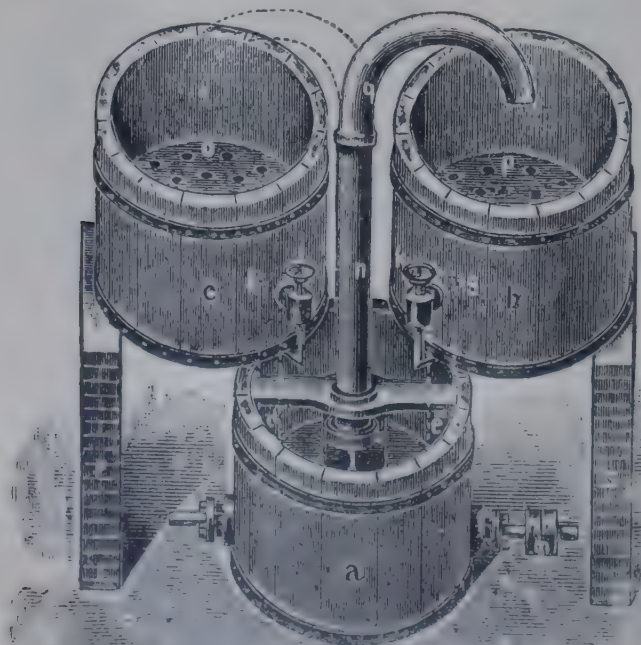


FIG. 213.—Dyeing Machine for Loose Wool, etc.  
(Schirp.)

Numerous machines have been devised in which the motion given to the rods by hand is imitated mechanically. The plan most suitable for mechanical treatment seems to be the employment of a wheel on which the hanks are suspended by means of two series of rods, one series fitted near the centre, the other on the circumference of the wheel. The latter partially dips into the dye vat, and in turning slowly, alternately dips the hanks into the liquor and then lifts them out to drain; at the same time the sticks receive a rotary motion. The whole wheel is advantageously enclosed in a case fitted with doors. Fig. 212 shows a machine of this kind constructed by the Klauder-Weldon Dyeing Machine Co. This machine may also be employed for dyeing slubbing (combed wool) in the hank.

**The Dyeing of Loose Fibre, Cops, etc.**—Loose fibres may be dyed in suitable boilers in which they are turned by hand by means of poles. The material,



however, shows a considerable tendency to felt under these conditions, and mechanical appliances are, therefore, to be preferred.

The Klauder-Weldon Co. recommend a machine similar in appearance to the one described above for the dyeing of hanks. In it the material is placed in a perforated drum or wheel, which is divided into four sections or compartments and made to rotate inside a case in a similar manner to the wheel referred to above. In doing so, it alternately dips the fibres into the dye liquor and lifts them out to drain. The plan adopted by nearly all designers of dyeing machines for loose fibres, however, consists in placing the material in a perforated vessel or cage and forcing the dye liquor through it by means of a circulating pump, or by some other means. In many machines the direction of circulation can be reversed at will in order to ensure perfect uniformity of penetration. As a rule cotton is packed more tightly than wool, and a greater pressure of the circulating liquor is therefore necessary. Fig. 213 illustrates a simple machine for the dyeing of loose wool, etc. The material to be dyed is placed in one of the tubs *b* or *c*, of which one may be charged while dyeing is proceeding in the other. These tubs are fitted with a false bottom. The dye liquor is made up and kept continually heated in the tub *a* placed below *b* and *c*. The interior of the tub *a* is provided with a cataract pump which delivers large volumes of liquor through the pipe *n* and the movable

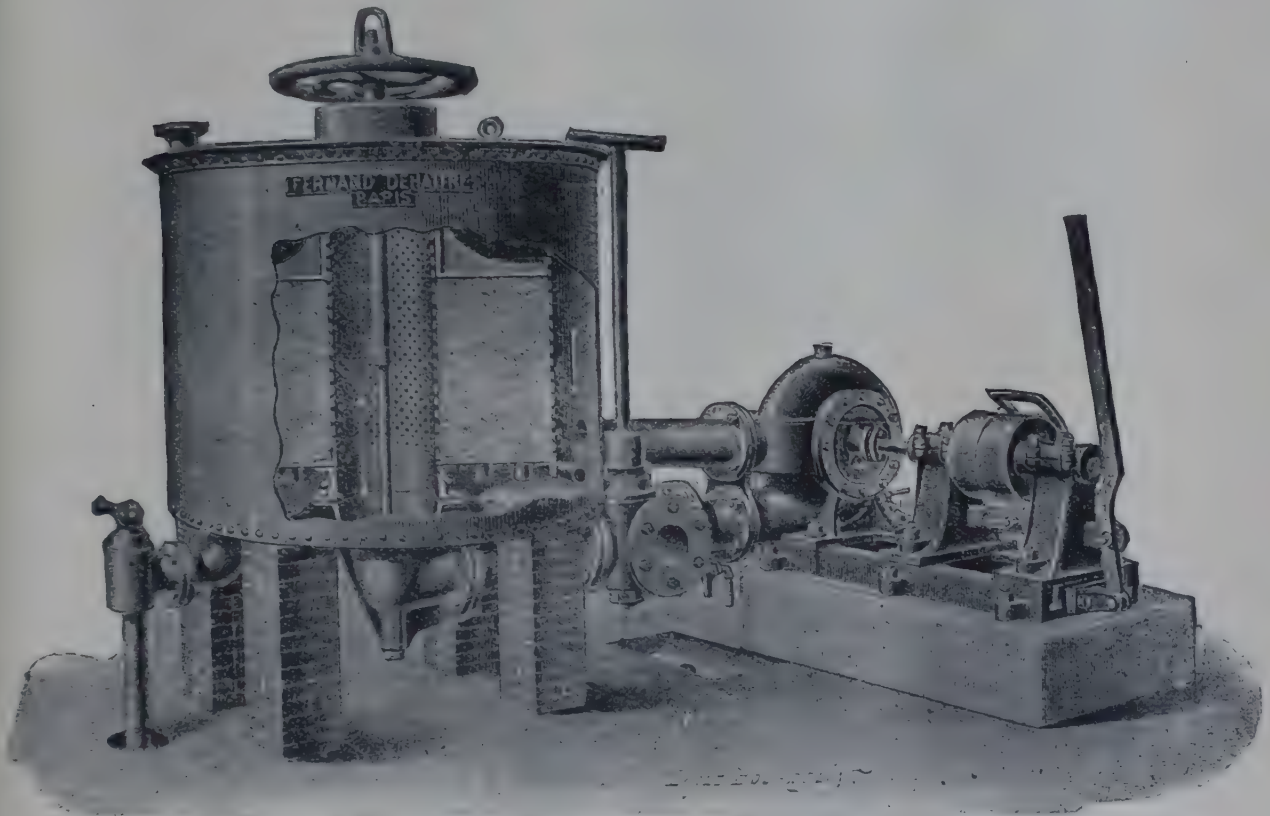


FIG. 214.—Dyeing Machine for Loose Fibres (Obermaier Type).  
(Dehaitre.)

connecting piece *g*. The latter may be turned so as to deliver on the top of the material contained in either of the dye vats *b* or *c*. This liquid then runs back again to the tub *a* through pipes fitted to the bottom of *b* and *c*, thus producing continual circulation. The goods are covered by a sieve and a spreader for the dye liquor, and the vats *a* and *b* are kept covered during use. This same apparatus may be provided with pipes to allow circulation of the liquid to proceed alternately from above and below.

A machine very frequently employed for the dyeing of loose cotton and wool is the Obermaier apparatus. In machines of this type (Fig. 214) the material is placed in a perforated drum, with a central perforated tube. This drum is fitted inside the dye tank proper, and can be removed at will for charging. Circulation of the liquor is produced by means of a centrifugal pump in the direction shown by the arrows.

Fig. 215 shows a machine charged with cops *u* and cross-wound bobbins *v*, which is also constructed in a slightly different manner for the dyeing of loose fibre. Like the Obermaier apparatus it consists, in the latter case, of a movable drum *I* for holding the material through which dye liquor is forced by means of the pump *G*. The drum is placed in the dye vat *B* which has a detachable front. In this apparatus the shell of the drum is not perforated, but it is divided into three compartments by perforated walls. The central compartment serves for distributing the liquor, the outer two for holding the fibre. The pump is double-acting, so that the direction of circulation can be reversed at will.



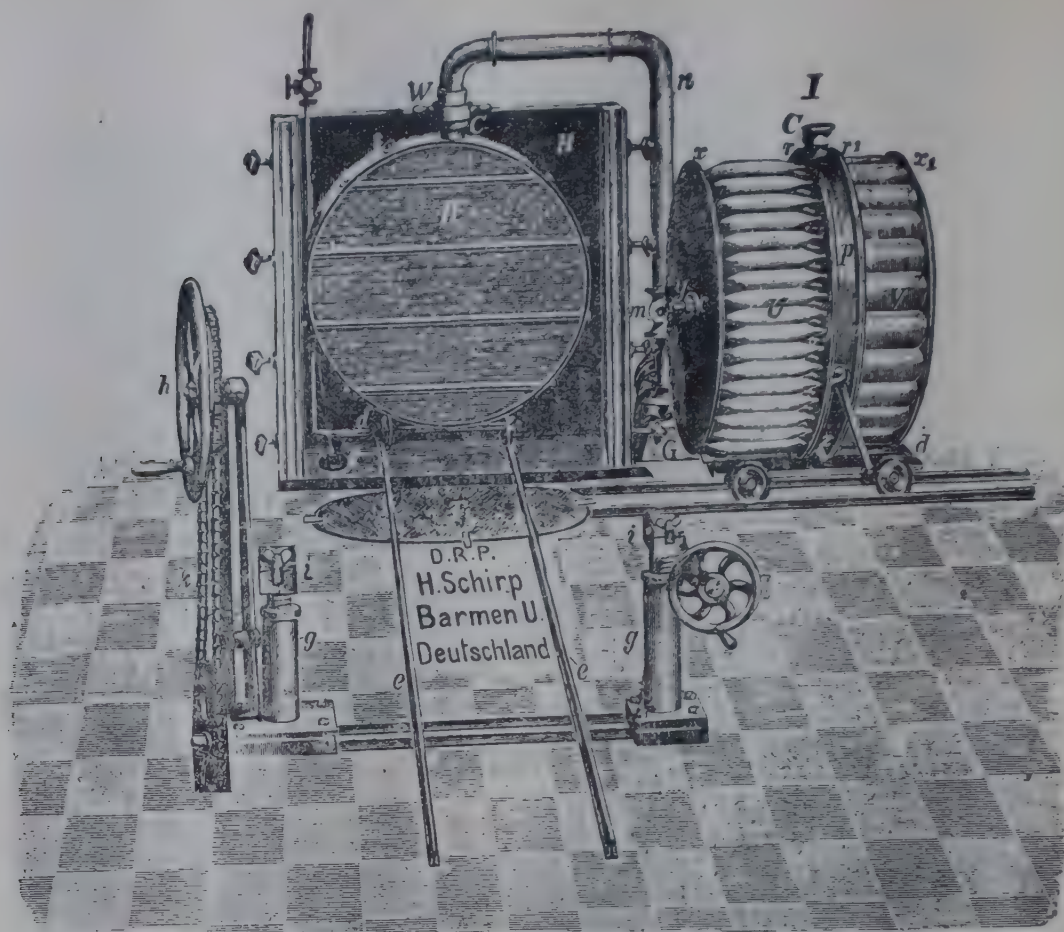


FIG. 215.—Dyeing Machines for Cops, Cheeses, etc.  
(Schirp.)

Cops and cross-wound bobbins may be dyed by the “packing” system in machines similar to those used for loose cotton. In this case solid wooden skewers must be inserted to prevent them from collapsing, and all spaces must be very evenly packed by means of some packing material such as loose cotton, etc. A method that leads to satisfactory results much more easily is the hollow perforated skewer system. In this system each cop or cross-wound bobbin is placed on a perforated paper tube on a perforated spindle or skewer, and the dye liquor is forced or sucked through the

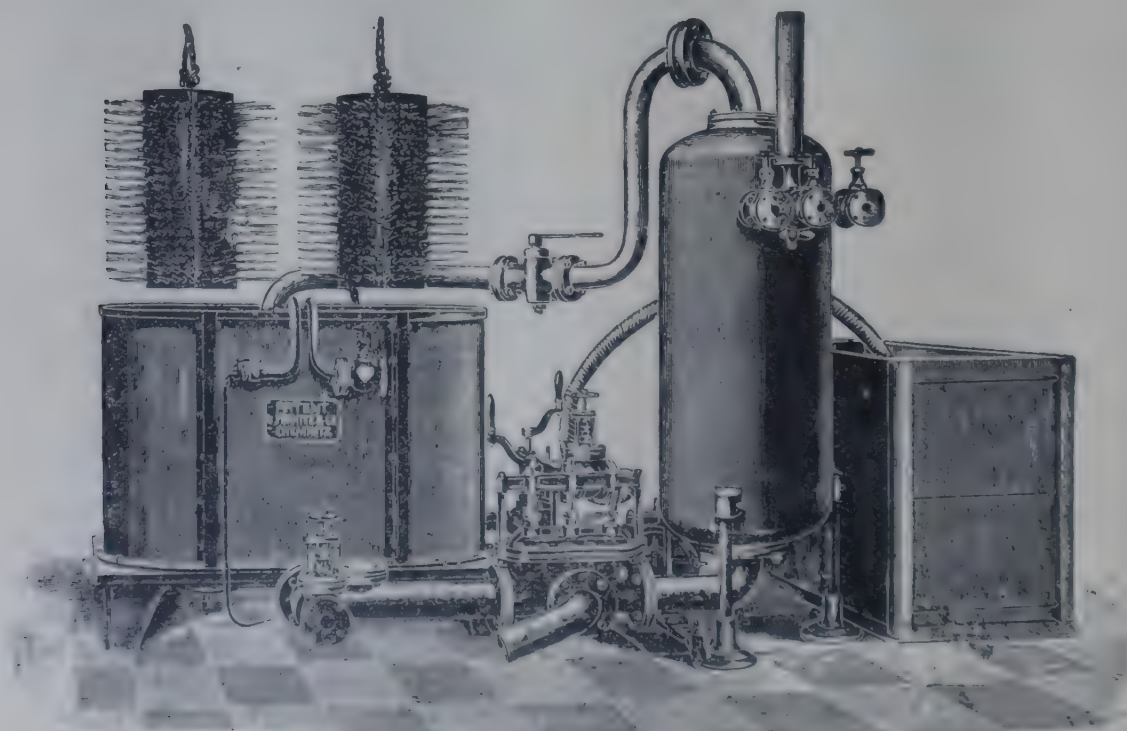


FIG. 216.—Dyeing Machine for Cops, Cross-wound Bobbins, Loose Fibres, etc.  
(Pornitz.)



cop either directly by means of a pump, or else compressed air or vacuum or steam is employed for this purpose. Fig. 216 illustrates a machine of this type in which the cops or cross-wound bobbins are mounted on cylinders. In the machine already described, Fig. 215, they are inserted between two perforated metal plates, and Fig. 217 illustrates a cop-dyeing machine in which the cops are mounted on a square perforated plate.

**Washing.** — After dyeing, the goods must in nearly all cases be washed in water. Machines of similar or of identical construction to those used in dyeing may usually be employed. In all those cases already described in which the liquor is circulated by means of a pump, the dye liquor is usually simply withdrawn from the vat without removal of the goods and replaced by water. Most of the washing machines described in the chapter on bleaching may also be employed by the dyer. In the washing of cotton piece-goods it is often desired to cause the scouring liquor to impinge with considerable force against the cloth. For this purpose so-called beaters may be employed. These may be described as scoops which rotate rapidly on the surface of the liquor and throw it with considerable force against the cloth. Fig. 218 illustrates the action of such beaters, and Fig. 219 shows a washing machine fitted with beaters. In this figure a vertical drying machine is also shown on the right. It will be seen that the calico passes through various tanks over guide rollers alternately placed in and above the liquid. Squeezing rollers are provided.

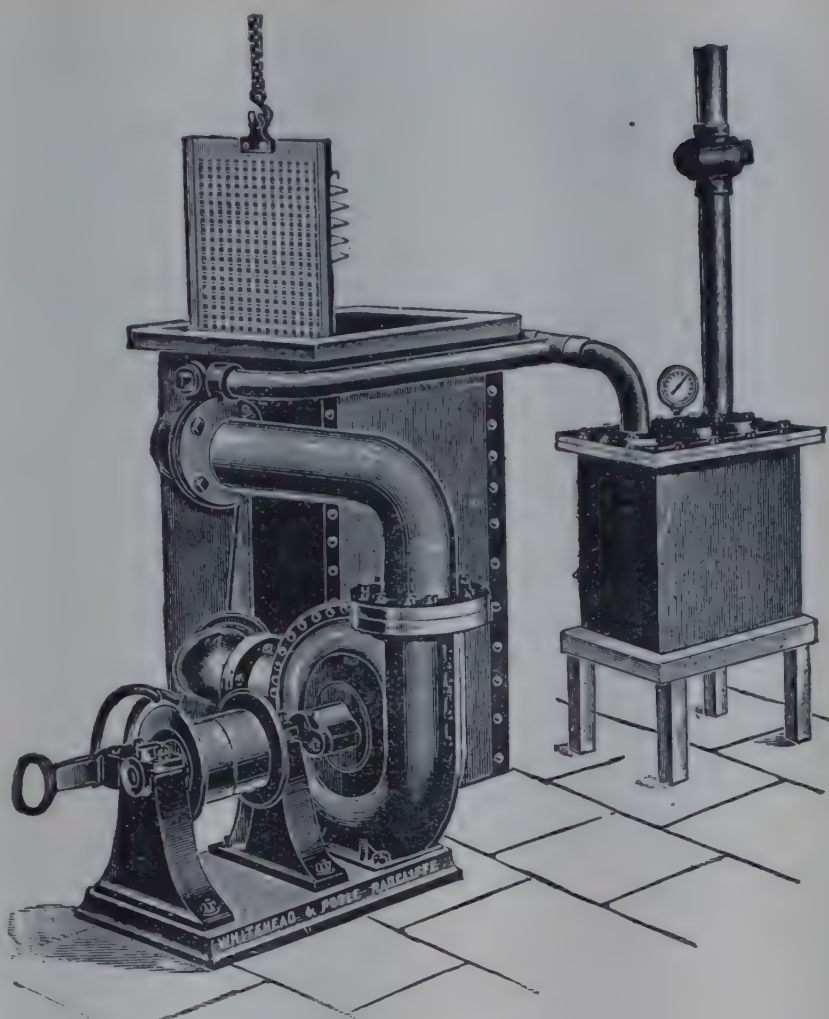


FIG. 217.—Cop-Dyeing Machine.  
(Whitehead & Poole.)

For this purpose so-called beaters may be employed. These may be described as scoops which rotate rapidly on the surface of the liquor and throw it with considerable force against the cloth. Fig. 218 illustrates the action of such beaters, and Fig. 219 shows a washing machine fitted with beaters. In this figure a vertical drying machine is also shown on the right. It will be seen that the calico passes through various tanks over guide rollers alternately placed in and above the liquid. Squeezing rollers are provided.

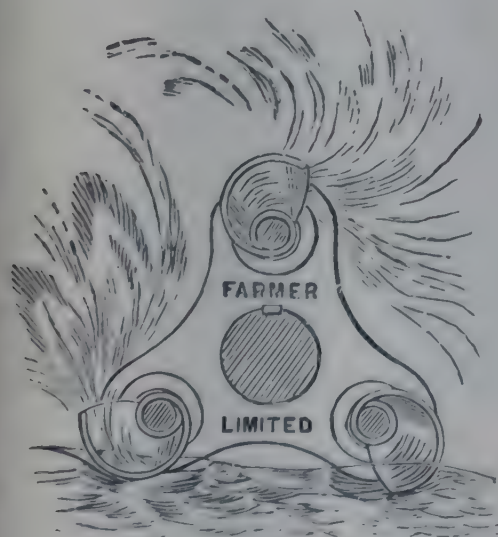


FIG. 218.—Beaters.  
(Farmer.)

**Drying.**—The process of drying may be said to consist of two operations, firstly, the removal of as much water as possible by mechanical processes, and secondly, the evaporation of the remaining moisture. The former operation may be carried out by squeezing or wringing. A more thorough method for the mechanical removal of liquid, however, consists in throwing off the drops by centrifugal force. For this purpose so-called hydro-extractors are employed. These are machines which consist essentially of a perforated metal cage for holding the goods, which can be rotated very rapidly around a vertical axis by an electric motor or otherwise



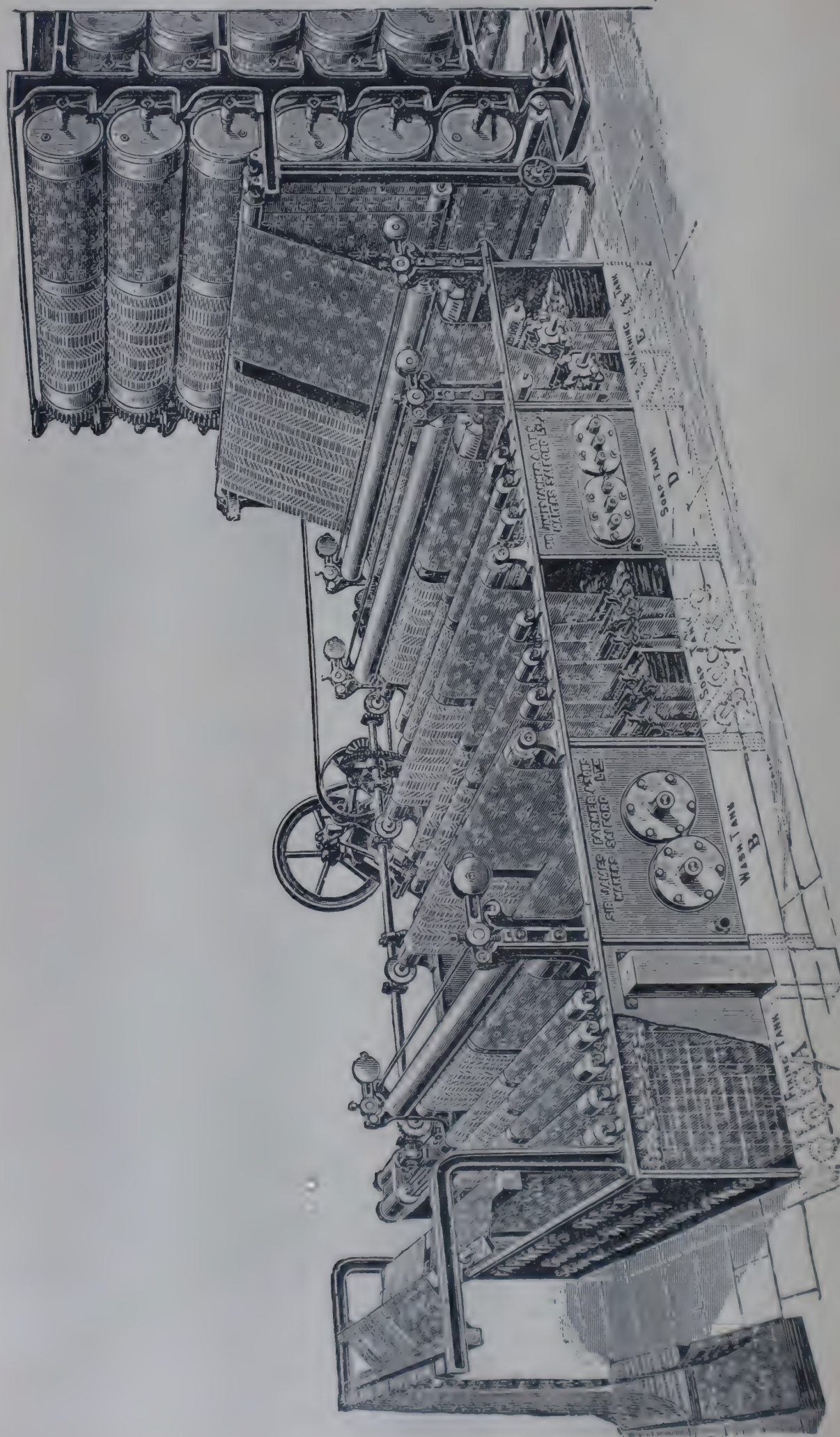


FIG. 219.—Washing Machine and Vertical Drying Machine. (Farmer.)



(see Figs. 220, 64, 65). The liquid is collected in a casing which usually forms part of the framework of the machine.

For the final drying of the fibres by evaporation, artificial heat is usually applied, although drying at ordinary temperature is sometimes carried out.

Loose fibres are usually dried in a machine consisting essentially of a chamber through which the fibres travel on an endless band, meeting a countercurrent of hot air during their passage.

Yarn is usually dried by suspending the hanks on poles or movable frames in specially constructed drying ovens through which a slow current of hot air is passed. Cops and cross-wound bobbins may be dried in a similar manner, or else the suction drying system may be employed particularly in conjunction with the machine shown in Fig. 217. The cops are left on the cylinders which are put in special machines in which hot air can be drawn through the cops.

Cloth is usually dried by passing it face upwards over steam-heated rollers (see Fig. 219). The final drying is frequently carried out in stentering machines (Fig. 221). In these the cloth which has shrunk slightly in the processes of dyeing is brought back to its original width by stretching slightly. For this purpose the moist cloth is passed between two moving endless chains which grip it at the selvages by means of clips. These chains are not parallel but diverge slightly so that the cloth is stretched during its passage between them. At the same time it is dried by hot air drawn over steam pipes.



FIG. 220.—Hydro-Extractor.  
(Dehaitre.)

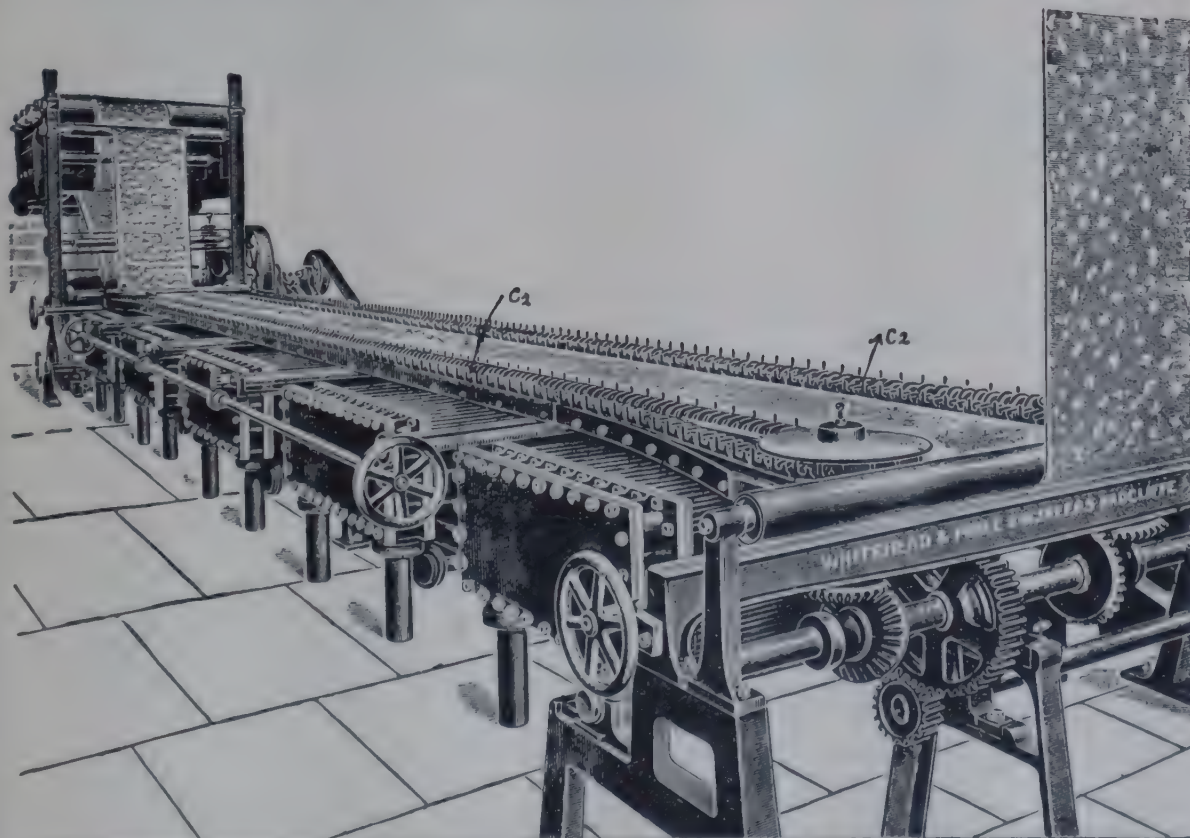


FIG. 221.—Clip Stenter with Hot-Air Drying Arrangement.  
(Whitehead & Poole.)



Before leaving the subject of dyeing machinery, a brief reference must be made to the **agers** employed particularly in the development of **aniline black**, pp. 480, 556 (and also for the fixation of printed colours). These consist of chambers containing a hot atmosphere heavily charged with steam in which the cotton cloth can be hung or through which it can be passed continuously over rollers. Fig. 222 illustrates a **rapid ager** for aniline black. It is fitted with heating coils and a perforated pipe for the supply of steam. The roof and the guide rollers near the common inlet and exit of the cloth are heated by steam to prevent the formation of drops of water which would soil the goods.

### Direct Dyes

The simplest dyes, from the dyer's point of view, are those which are taken up directly from their solutions by the fibre.

**Direct Cotton Dyes.**—During the last three decades a large number of direct cotton dyes have been put on the market. The dyes of this class appear to belong to a few well-defined groups of chemical compounds. We have firstly the congo-red group, the members of which contain the tetrazo grouping of atoms

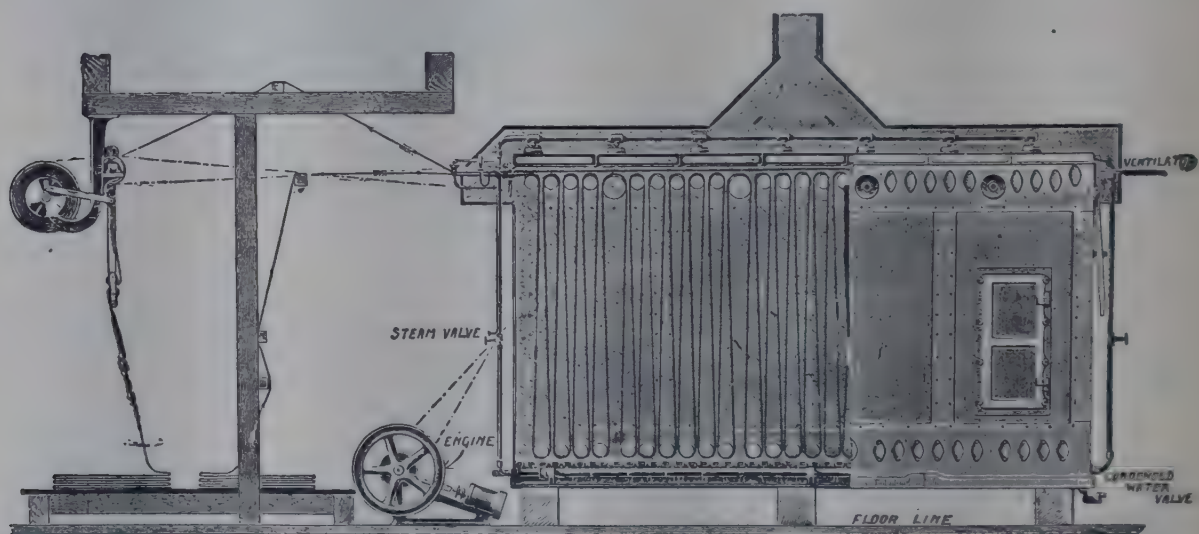


FIG. 222.—Rapid Ager. (Mather & Platt.)

$\begin{Bmatrix} -N=N- \\ -N=N- \end{Bmatrix}$ ; secondly, the *primuline group*, which appear to have the radicle  $\begin{array}{c} S \\ \diagup \quad \diagdown \\ - \quad C - \end{array}$  in common; and thirdly, various dyes, which may be classed as *di-stilbene-azo-dyes*. Most of these dyes are also taken up by wool and silk, but a few, notably members of the last-named group, hardly dye the animal fibres at all. The direct cotton dyes are thus of particularly great importance for the dyeing of union goods, satins, etc.

The fact that these substances are not taken out of the dye-bath with the same degree of avidity as direct dyes for wool and silk, and that the process of absorption is of a more or less reversible nature, has already been referred to in the Introduction. On account of these circumstances they eminently show the desirable property of "level dyeing," but also exhibit to a marked extent an undesirable tendency towards "bleeding" or "running." It follows also that they must be dyed from as concentrated a solution as possible (weight of solution, say, ten to thirty times that of the cotton), and varying quantities of salts, such as sodium sulphate or common salt, are added to aid in the exhaustion of the dye bath. Since these colours are dyed in a neutral or alkaline bath, and most of them are precipitated by lime or magnesia, it is necessary to soften hard water before use. This is most conveniently done by



boiling with a small amount of soda ash. As a rule the goods are entered at medium temperature, and dyeing is carried on at the boil, but dyeing at low temperatures is also sometimes carried out. The dye baths are not exhausted, and may be used over again after making up to strength by the addition of the necessary amount of dyestuff.

The following are two of the processes which may be employed :—

**1. Process at Boiling Temperature.**—Work the cotton at the boil for one to one and a half hours, adding 5-30 per cent. (on weight of cotton) of crystallised Glauber's salt, or  $2\frac{1}{2}$ -10 lbs. of common salt.

The salt aids in the exhaustion of the bath but rather hinders boiling, and if difficulties are met with in this respect its quantity must be reduced, or it must be replaced by soap, turkey red oil, etc. After removal from the bath the goods are wrung and then rinsed in cold water, soda solution, or turkey red oil.

**2. Cold Bath.**—Stir the dyestuff with an equal weight of caustic soda solution of sp. gr. 1.35-1.38 ( $70$ - $76^{\circ}$  Tw.), and dissolve the whole in boiling water. Enter the cotton into the bath when cold or lukewarm and dye with the addition of a little soap and, if necessary, Glauber's salt.

The following are some of the names and prefixes employed by various firms to indicate their direct cotton colours: Benzo-, Congo-, Diamine, Union, Direct, Purpurine, Diamol, Chlorazol, Ingrain, Sultan, Titan, Primuline, Sulphine, Oxamine, Pyramine, Thiazine, Phenamine, Chrysamine, Oxyphenine, Chrysophenine, Curcumin, Zambesi, Chicago, Columbia, Hessian, Triazol, Toluylene, etc.

**After-treatment of Direct Cotton Dyes.**—The direct cotton dyes are eminently suitable for after-treatment on the fibre, whereby not only new shades are produced but very much faster colours are obtained.

Basic dyes may be dyed upon them as on mordants (p. 549), or they may be converted into new "ingrain" colours by the process of diazotising or coupling (pp. 442, 450, 478, 558).

Many of them are also greatly improved by after-treatment with metallic salts, such as copper sulphate, chromium salts, and the bichromates of sodium and potassium (p. 553).

Another method of after-treatment which has a marked effect on the fastness to washing and milling of certain dyes consists in working the dyed cotton for about half an hour at  $60^{\circ}$  in a bath charged with 1-3 per cent. formaldehyde (40 per cent.).

**Wool and Silk** are both frequently dyed with the direct cotton colours, the former in neutral or very feebly acid baths containing Glauber's salt at boiling temperature, the latter in a neutral boiled off liquor bath, the fibre being entered at lukewarm temperature and the bath being gradually taken to boiling temperature. After dyeing has proceeded for about an hour, the bath is usually made feebly acid with acetic acid to aid exhaustion.

The dyes may be subjected to after-treatment as on cotton, and the silk is finally brightened by passing through a very dilute solution of acetic or tartaric acid \* and dried without washing.

## Sulphur Colours

The sulphide or sulphur colours which have become of great importance in recent times for obtaining fast shades on cotton or other vegetable fibres, form a group of dyes that are obtained by fusing sodium sulphide, or a mixture of sodium sulphide and sulphur with various organic substances. They are insoluble in water and are dyed from a solution in sodium sulphide. Many of them are reduced by the bath and presented to the fibre as more or less coloured leuco compounds, being afterwards oxidised by contact with the air. They will readily dissolve in alkaline reducing agents, and may occasionally be dyed in the vat like indigo.

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\* The brightening of silk by treatment with acid is due to the fact that silk absorbs acid and retains it tenaciously, whereby its lustre is increased and it acquires the property of emitting a crackling sound called the scroop of silk when it is twisted and pressed together. The rustling of silk garments is doubtless due to this property. Tartaric acid being retained more permanently than the other acids, is the most efficient, but the most expensive of the acids employed.



They may be employed for dyeing artificial silk and also silk and wool, but the animal fibres, more especially wool, are liable to attack by the alkaline sulphide solutions unless protected by special previous treatment. The dyes are occasionally employed in the dyeing of unions. These colours are distinguished by good fastness to light, washing, cross-dyeing, etc., and they do not bleed like the direct cotton colours.

It has occasionally been observed that the cotton fibre has become tendered on storing after dyeing with the sulphur colours, and this has always been associated with the formation of sulphuric acid. When this difficulty occurs, it is best met by subjecting the cotton to an after-treatment with a feebly alkaline substance, such as soap, sodium acetate, or carbonate. A very suitable process appears to be that recently patented by Holden, in which calcium tannate is deposited on the fibre after dyeing, by steeping the material for a few minutes in tannic acid at about 40° C., squeezing, passing through limewater, and washing. The calcium tannate being insoluble has the advantage of not being liable to be removed on washing like the feebly alkaline substances mentioned above. After dyeing, the material should in all cases be wrung well and rinsed thoroughly.

In dyeing with these colours, vats made of wood or iron may be employed. Copper or any alloys containing this metal must be carefully excluded, as this metal goes into solution rapidly in the sodium sulphide solutions, and the copper compounds formed, lead to oxidation of the dyestuff and irregular dyeing. The fibre should be kept submerged, and yarn may conveniently be dyed on bent iron pipes, the ends of which have been wrapped round with cloth.

The dyestuff, to which has been added about three or four times its weight of crystallised sodium sulphide and some soda ash, is dissolved in a small amount of boiling water with stirring, and the solution obtained, is added to the bath, which usually contains an amount of water equal to about twenty to thirty times the weight of the cotton. The amount of soda ash employed is about 5 per cent. of that of the cotton, and the bath contains 10-60 per cent. (on the weight of the cotton) of common salt according as a light or dark shade is required. For dark shades the cotton may be entered at boiling temperature, turned several times, and allowed to steep for several hours. For lighter shades a lukewarm or even a cold solution may be employed and a shorter time is requisite. Turkey red oil is sometimes added to the bath to secure more even dyeing. Certain sulphur dyes, such as the kryogene blues, must be developed by oxidation in air at a high temperature in the presence of moisture, by steaming in the presence of air, or by storing in a damp warm place.

An after-treatment with oxidising metallic salts, viz., with a solution containing, say, 2 per cent. of potassium bichromate, 2 per cent. of copper sulphate, and 3 per cent. of acetic acid on the weight of the cotton at about 70° C. improves the fastness of some of these dyes.

Like the direct cotton colours they act as mordants for basic colours, and many of them may be coupled with diazo solutions (p. 558). The first dye of this description known, viz., Cachou de Laval, was discovered a considerable number of years ago. The following are some of the names employed by various firms to indicate the newer sulphide dyes: Amidazol, Crossdye, Immedial, Katigene, Kryogene, Pyrogene, Sulphur Thiogene, Thion, Thionol, Thioxine.

**Natural Direct Dyes for Cotton.**—Several natural dyes, such as turmeric, safflower, and annatto, are direct dyes for cotton.

## ACID DYESTUFFS

This class comprises all those dyestuffs which are of an acid nature. It is obvious that some of these colours may belong to the class of direct cotton dyes, others may often be employed in conjunction with mordants, and thus the various classes of dyes merge into each other. The acid dyes are either nitro compounds or sulphonic acids, and in nearly all cases they are sold in the form of sodium or occasionally calcium salts. In many cases they have been obtained from basic dyes by introducing the sulphonic group of atoms.

**Cotton.**—Generally speaking the acid dyes will only stain cotton and other vegetable fibres very slightly, so that only very light and fugitive shades can be obtained by direct dyeing even when concentrated baths are employed. The results



are somewhat better when the dyes are used in conjunction with gelatine or basic mordants, such as alumina or stannic oxide, but even so, the shades obtained are not fast to washing.

**Wool.**—The acid dyes are of the very greatest importance in the dyeing of wool. The wool is always dyed at boiling temperature, and a quantity of sulphuric acid is usually added, which is very much in excess of what is required to liberate the free colour acid from its salt. That the object of this acid is to produce lanuginic acid from the wool, which latter substance is primarily dyed, has already been mentioned in the Introduction. The mineral acid might thus be termed a "mordant" (*i.e.*, biting agent), using the word in the significance in which it was originally, though wrongly, employed by the dyers of former times.

Sodium sulphate or bisulphate is nearly always added as a levelling agent, since this substance appears to have a slight solvent action on the dye taken up by the fibre, thus removing it from those places in which it may have been deposited in excess, and generally retarding the operation of dyeing. When dyestuffs are employed which dye with exceedingly great rapidity, the sulphuric acid is replaced by acetic acid or by ammonium sulphate or acetate, substances which slowly become acid in the boiling bath owing to the expulsion of ammonia. In certain cases, particularly in the dyeing of unions, a boiling neutral bath is employed. Stannic chloride or alum is sometimes added in small quantity; tin oxide or alumina will thus be deposited on the fibre from the boiling bath, and by taking up colour from the solution increase the brilliancy of the shade. Certain acid dyestuffs, *viz.*, the alkali blues, are not soluble in dilute acids and must be dyed from a feebly alkaline solution. The wool is afterwards treated in a hot bath containing dilute sulphuric acid. The colourless sodium salt which is originally taken up is thus converted into the blue acid.

The following may be taken as an example for the dyeing of 100 kg. of wool.

Employ a bath (5,000-10,000 l.) containing 1-4 kg. of concentrated sulphuric acid, 10-20 kg. of Glauber's salt crystals and the requisite amount of dyestuff, enter at about 70° and heat to the boil, leaving the wool in the boiling bath for about an hour.

**Silk.**—The acid dyes are of considerable importance in silk dyeing, although they are not fixed so well as on wool.

A bath is usually employed containing 20-30 per cent. (on volume of bath) of boiled-off liquor, which is slightly acidulated with sulphuric or acetic acid. The silk is usually entered at lukewarm temperature and dyed slightly below boiling. It is then washed with water and brightened by means of sulphuric, acetic, or tartaric acid, and dried without further washing.\*

The following are a few of the more important names met with among the acid dyes: Naphthol yellow, Tartrazin, Fast yellow, Tropæolin, Brilliant orange, Brilliant scarlet, Xylidine scarlet, Biebrich scarlet, Croceïn scarlet, Fast red, Archil substitute, Orseillin, Acid magenta, Acid eosin, Acid rhodamine, Acid phloxin, Acid violet, Alkali violet, Sulphone azurin, Alkali blue, Soluble blues, Patent blue, Cyanine, Soluble induline and nigrosine, Naphthazine blue, Wool green, Naphthol green, Fast brown, Orcellin, Naphthol black, Naphthylamine black, Sulphone black, Wool black, Biebrich patent black.

## BASIC DYES

This important class, which comprises some of the most brilliant and beautiful colours known, consists of coloured salts of colourless acids and organic colour bases. When the animal fibres are dyed by these substances, only the base is taken up in a coloured form, as explained in the introduction, the acid being left behind in the bath.

**Cotton.**—Cotton is nearly always dyed with the intervention of an acid mordant, and the processes employed will, therefore, be considered later in conjunction with those used for mordant dyes (pp. 548, 550).

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\* See note, p. 545, also see p. 518.



**Wool.**—Although not so important as the acid dyes on account of their fugitiveness, yet the basic dyes still possess a considerable amount of importance in the dyeing of wool. They are in most cases dyed from a very feebly acid bath, but a soap bath is also sometimes employed when very soft water is available. That hard water must be feebly acidified, preferably by acetic acid, has already been mentioned under the heading of **Water**. No other addition is made.

The bath is usually started cold and gradually raised to the boil. Dyeing is continued until the bath is exhausted, which sometimes takes place before boiling. The goods are well washed after dyeing. Owing to the great tinctorial power of these dyes a very small amount is usually sufficient,  $\frac{1}{2}$  per cent. on the weight of the wool usually producing a medium shade. The colours should be filtered through cloth before adding to the dye bath as a precaution against the introduction of undissolved particles.

**Silk.**—On account of their brilliance the basic dyes play an important part in silk dyeing in spite of their fugitiveness as a class. A neutral or slightly acid bath may be employed consisting of one-third boiled-off liquor and two-thirds water. The same general precautions must be taken as in the dyeing of wool.

The silk is usually entered cold and the temperature gradually raised to a little under boiling. After dyeing, the fibre is rinsed and brightened by means of tartaric or acetic acid.\*

A bath containing about  $1\frac{1}{2}$ -2 per cent. (on the weight of the silk) of soap is frequently employed for dyeing pale shades at a temperature of  $30^{\circ}$ - $40^{\circ}$  C. ( $85^{\circ}$ - $105^{\circ}$  F.).

The following are a few of the best-known basic colours: Magenta, Safranine, Magdala red, Chrysoïdine, Phosphine, Auramine, Methyl green, Malachite green, Diphenylamine blue, Victoria blue, Methylene (ethylene) blue, Meldola's blue, Nile blue, Indulines and Nigrosines, Methyl violet, Crystal violet, Mauve, Bismarck brown, Fast black.

The rhodamines, including irisamine, etc., also belong to this group, and the weakly acid eosins, including erythrosin, phloxin, rose bengal, may be dyed by similar methods.

## MORDANT DYES

The mordant dyes are basic or acid substances which are not fixed on the fibre directly, but are caused to combine with a compound of an acid or basic nature termed a mordant which has usually been previously deposited on the fibre. The compound formed is termed a colour-lake.

Some dyes, such as alizarin or logwood, are only feebly coloured before combination, and yield different shades with different mordants. These are termed **polygenetic dyes**. Others have the property of dyestuffs before combination, and their lakes do not usually differ much from them in colour. These are "**monogenetic**" dyes.

**Acid Mordants.**—These mordants are of the greatest importance for the fixation of basic dyes, particularly on cotton. They are also frequently employed in order to fix basic mordants on other fibres, and in silk weighting. The most important are the tannins and the oil mordants.

The **tannins**† form a class of compounds which are distinguished by the fact that they are taken up readily by the animal skin, causing it to be tanned. Most of them are colloids, and their more important properties are doubtless closely connected with this circumstance. They will combine with basic dyes producing compounds insoluble in water but soluble in an excess of tannic acid. When brought together with salts of heavy metals containing a feeble acid a precipitate is formed containing the metal oxide and the tannin. This precipitate which is insoluble in tannic acid is probably what is termed a colloid compound, *i.e.*, a compound produced by the phenomenon of "adsorption" between a colloid bearing a positive and a colloid bearing a negative electric charge when in solution. These precipitates have the property of combining with basic dyes, forming the coloured so-called "triple" compounds which constitute the lakes employed in dyeing cotton with basic dyes.

\* See p. 545.

† See also pp. 490 and 573.



The most important tannin is tannic acid or gallo-tannic acid, a substance obtained commercially on the large scale by the extraction of nut galls. This substance should be exclusively employed for dyeing pale shades on cotton; for dark shades the more or less coloured extracts of the following substances containing tannin may be employed—sumach, myrobalans, divi-divi, valonia, chestnut, etc. The bath is prepared according to the amount of colour to be fixed with quantities of tannic acid, varying, say, from  $\frac{1}{2}$ -8 per cent. on the weight of the cotton, allowing sufficient water to work the material conveniently. For pale shades the material, which must have been carefully freed from air by boiling out, is worked for a half to one hour in the bath; for darker shades the material may be entered at boiling temperature and then allowed to steep in the cooling bath for twelve hours. It is then worked in a tartar-emetic bath containing, according to the amount of tannin to be fixed,  $\frac{1}{2}$ -4 per cent. (on the weight of the cotton) of tartar-emetic for about a quarter of an hour. The insoluble antimony tannin compound referred to above is thus produced. The excess of antimony salt must be very carefully washed out or preferably removed by passing the dyed goods through another tannin bath. Aluminium, iron, or stannic salts are also employed for the fixation of tannic acid.

**Turkey-red oil, Alizarin oil, Sulphated oil, Soluble oil,\*** are names applied to another class of acid mordants which are sometimes employed for fixing basic dyes on cotton. Their principal importance, however, lies in their application to the fixation of basic mordants in turkey-red dyeing. As will have been seen from the prescriptions given for dyeing with various direct dyes, turkey-red oil is also frequently employed as an assistant in the place of sodium sulphate where difficulties are met with in obtaining level shades.

Turkey-red oil is formed by the action of concentrated sulphuric acid at medium temperatures on various oils, such as olive oil, cotton-seed oil, and castor oil. The last-named is by far the most important. The products formed are distinguished by the fact that they are soluble in water, while they retain to a certain extent the properties of the oils from which they have been produced. Chemically, turkey-red oil is probably a mixture of various primary ethereal salts of sulphuric acid. It has the great advantage over ordinary soap that its salts with the alkaline earths are not sticky substances but fine powders which have no tendency to cause uneven dyeing.

In mordanting cotton, the material may be saturated with a solution containing 50 g. of turkey-red oil per litre, wrung, dried, and then treated for half an hour in a tepid solution of aluminium acetate of sp. gr. 1.015 in order to fix the mordant.

**Dyes as Mordants.**—The fact that basic dyes may be dyed on cotton on other dyes, which may thus in a certain sense be considered to be acid mordants, has already been referred to (pp. 545, 546).

**Dyeing Basic Dyes on Cotton.**—The basic dyes are usually dyed on mordanted cotton in the cold or at temperatures up to about 70°. A feebly acid substance, such as acetic acid or alum, is usually added to retard dyeing in order that even results may be obtained, and the dye solution is usually added during dyeing in intervals of about a quarter of an hour in about three or four portions. The operation is usually started in the cold and completed at about 60° C.

**Catechu.†**—In conjunction with the tannins reference must here be made to the exceedingly important natural dyes, catechu or cutch and gambier. These substances contain varying amounts of a tannin called catechutannic acid and a white crystalline substance known as catechin. In addition they contain a brown dyestuff formed by oxidation of the preceding.

Cutch and gambier are employed largely in cotton and to a certain extent also in wool dyeing. The material is usually immersed in a boiling bath of the dye containing about 10 per cent. of copper sulphate (of the cutch employed). The latter acts as an oxidising agent and probably also as a mordant. The material is then allowed to steep for several hours and afterwards treated with a hot bath containing about 2 per cent. of dichromate. This substance effects a further oxidation.

Catechu and gambier are also used in large quantity in silk weighting.

\* See p. 43.

† See p. 486.



### Dyeing in Conjunction with Basic Mordants

Nearly all insoluble metal hydroxides may be deposited on the textile fibres as mordants, for the purpose of obtaining colour-lakes with various dyes. A brief survey of the more important methods employed for the various classes of fibres, and a short reference to the dyes used, some of which are among the most important known, is all that can be attempted here.

**Wool.**—Wool is capable of dissociating the salts of heavy metals at boiling temperature, taking up both the metal hydroxide or a basic salt and the acid, the former in an insoluble form, the latter in a form in which it can be washed out by water. This fact is made use of in the mordanting of wool. It is necessary to employ such salts as are not dissociated hydrolytically by the boiling water to an appreciable extent or else to hinder this dissociation by the addition of suitable substances. The deposit of metal hydroxide formed would otherwise not be held fast by the fibre. Thus in mordanting with aluminium sulphate it is necessary to make an addition of sodium bisulphate, sulphuric acid, or preferably of cream of tartar or of some other substance of an acid nature.

The following prescription for alumina may be taken as an instance of the mordanting with salts such as aluminium sulphate, chromium fluoride, ferrous sulphate, etc. Employ a bath containing about 8-10 per cent. of alum and  $2\frac{1}{2}$ -5 per cent. of tartar (on the weight of the wool), enter at a low temperature, heat gradually to boiling and maintain at the boil for about half an hour. After cooling, the wool is thoroughly washed or preferably boiled in water to remove as much of the acid as possible. It is then dyed without allowing it to dry.

A very important mordant for wool that calls for a few special remarks is potassium (or sodium) **bichromate** (bichrome or chrome). The substance to be deposited on the fibre in this instance is chromic oxide, and reduction of the chromate originally taken up is therefore necessary. When chromate alone is employed, this reduction is probably effected to a small extent by the wool itself. The latter, however, still shows the yellow colour of chromate on leaving the mordanting bath, and the principal reduction no doubt takes place in the dye-bath later on.

It will be readily understood that care is necessary in the use of this mordant owing to its oxidising properties in order that "overchroming" of the wool may be avoided. According to Knecht, the chromate is taken up by the wool as chromic acid, and the bath consequently shows a tendency to become alkaline. If used over again it should therefore be made up to strength by the addition not only of bichromate, but also of the necessary amount of sulphuric acid.

For high-class goods bichromate is frequently employed in conjunction with reducing agents, of which cream of tartar, oxalic acid, formic acid, and lactic acid are the more important.

The following may serve as a prescription for the mordanting of wool with bichromate. Boil the wool in a bath containing 2-4 per cent. bichromate (of weight of wool). Water, fifty to a hundred times the weight of the wool. Time, one to one and a half hours; then wash with water and dye without drying.

**Basic Mordants for Silk.**—Silk is usually mordanted at medium temperatures at which the metal salts employed are not decomposed by the fibre. It thus becomes necessary to pass the latter through the solution of a fixing agent, such as sodium silicate, which deposits an insoluble basic precipitate on the silk. Instead of this, the fibre may in many cases simply be washed very thoroughly with water, which produces an insoluble precipitate by the process of hydrolysis. In the mordanting of silk with iron and tin salts tannin is usually employed as a fixing agent. A soap bath also has a similar effect. By passing the fibre alternately through baths containing the metal salt and the tannin extract, the fibre may be "weighted" up to about four times its weight with the metal tannate. This fact is made use of in dyeing silk with heavy logwood blacks.



**Basic Mordants for Cotton.**—Although cotton may absorb a certain amount of metal salts, it can in no way decompose them. Either a salt such as the acetate must be employed which can be decomposed or hydrolysed by heating, yielding a basic salt; or else a fixing agent, *i.e.*, a substance which yields a precipitate of basic properties when added to a solution of the salt in question, must be employed.

In the former case the impregnated goods are subjected to the process of “ageing,” which consists in exposing them to a warm moist atmosphere.

In the latter case the cotton may either be treated with tannin or some other acid mordant taken up directly by the fibre and then be passed through an alkaline bath and through the metal salt solution, or else the material is first passed through the metal salt solution and then treated with a fixing agent, such as ammonia, caustic soda, chalk, sodium carbonate, silicate, phosphate, or arsenate, which yields a precipitate of strongly basic properties by interaction with the salt in question.

When employing turkey-red oil or tannic acid, the cotton is first impregnated as described under acid mordants, it is then usually passed through clear lime water to neutralise the acid and afterwards worked in the salt solution for about an hour. It is usually finally passed through a weak soap bath, thoroughly rinsed in water, and then dyed.

When one of the alkaline fixing agents indicated above is employed, the cotton is usually treated for several hours with the mordant solution, wrung out, dried at a low temperature, then worked for about half an hour in the solution of the fixing agent at medium temperature, thoroughly washed, and then dyed.

### The Dyes

Although mordant dyes, both natural and artificial, are among the most important known, yet all that can be attempted here, is a brief enumeration of them, and an indication of the mordants with which they are applied.

**Logwood.**—This substance consists of the heart-wood of a tree known botanically as *Hæmatoxylon campechianum* which grows in various parts of America. The wood is subjected to a process of fermentation and oxidation called “ageing” or “maturing,” during which a glucoside originally present in it is decomposed into a sugar and a substance called hæmatoxylin. The latter on oxidation yields a body named hæmatein which is the colouring principle of logwood. The dye is bought by the dyer either as chips, as decoctions, known as logwood liquor, or as extract, *i.e.*, a paste obtained by evaporating the decoction. In the former case it is extracted by the dyer himself by means of boiling water. Logwood is employed for dyeing both vegetable and animal fibres, and its importance lies chiefly in the production of fast blues and blacks on the latter (see also pp. 484, 490).

When employed for dyeing blacks on cotton it is usually applied in conjunction with an iron mordant fixed by tannin.

The following prescription may serve as an example. Work the cotton in a cold infusion of about 30-40 per cent. of sumach (of weight of fibre), allow to steep for several hours, and without washing work for about half an hour in a cold solution of “nitrate” of iron (*i.e.*, ferric sulphate), sp. gr. 1.01-1.02, treat with a cold chalk bath to remove excess of acid, and wash thoroughly. Dye in a bath containing logwood and a little fustic (say 8 per cent. solid logwood extract and 1½ per cent. of fustic extract of sp. gr. 1.25), then treat with a bath of about 1½ per cent. copperas, or with a warm bath containing potassium bichromate (say ½ g. per litre) in order to remove the excess of logwood. Then work in a solution of soap, say 5 g. per litre, at a moderate temperature, squeeze and dry.

Chrome blacks may also be obtained on cotton; a purple is obtained by means of a tin, a blue by means of a copper mordant.

**Wool** is dyed black by means of either an iron or chrome mordant.

The following prescription may serve as an example. Mordant in a bath containing 3 per cent. potassium bichromate, 8 per cent. tartar, and 5 per cent. sulphuric acid (of weight of wool) at boiling



temperature for about an hour, wash well and dye in a boiling bath prepared from 50-80 per cent. logwood and 5-10 per cent. fustic for about an hour, having entered the wool at about 80° C. An addition of about 5 per cent. alizarin improves the fastness of the shade to light. Then fix the excess of logwood taken up in a finishing bath containing about 1 per cent. of potassium bichromate at about 80° C. Wash and dry.

In order to produce logwood blues on wool, smaller quantities of dye and mordant are employed, and the fustic is omitted in the dye bath.

**Silk.**—Logwood blacks play an important part in the dyeing of silk. As a rule the logwood is dyed on an iron tannin mordant, and other substances are incorporated with the dye, allowing it to weight the silk up to about 400 per cent.

The following prescription, by means of which iron tannate, tin tannate, Prussian blue, catechu, and logwood are all fixed on the fibre, allows a weighting up to about 100 per cent. and may serve to illustrate the process.

Mordant with basic ferric sulphate, then soap. Repeat these operations one to eight times, according to the amount of weighting desired; dye Prussian blue by means of potassium ferrocyanide, treat with a catechu bath (100-150 per cent.) containing 10-15 per cent. stannous chloride at 60°-80° C. Treat with a second catechu bath containing no tin (100-200 per cent. catechu), mordant with pyrolignite of iron. Dye with logwood and soap. Brighten.

The following **natural mordant dyes** can only be referred to: Fustic (young fustic) and Quercitron bark (yellow on chromium mordant); Weld (yellow on chromium, aluminium, tin;—olive or olive-yellow on iron and copper mordant); Persian berries (yellow or yellowish olive on tin, copper, aluminium, iron;—brown on chromium mordant); Saunders wood, barwood, camwood (red to brown according to mordant); Cochineal, Kermes, and Lac dye (scarlet and crimson on tin and aluminium mordant) (see also **Natural Dyes**, p. 483).

**Alizarin.**—This exceedingly important dyestuff, which constitutes the principal colouring matter of madder, is at the present time obtained practically exclusively by artificial means from coal-tar (p. 451). The two substances, isopurpurin and flavopurpurin, are present in varying amounts in different brands of the commercial article and affect the shades of the dyed material to a certain extent. Alizarin is put on the market as a paste containing 20 or 40 per cent. of the dyestuff or as a powder containing from 80 per cent. upwards. Its most important application is the production of turkey red on cotton.

It would be beyond the scope of this article to give a full account of turkey-red dyeing, but it may be stated briefly that the production of this exceedingly brilliant and fast colour is based on the formation of an exceedingly complicated aluminium-calcium lake of alizarin which contains also a certain amount of tannin and oil. The latter is a decomposition product obtained by using either olive or turkey-red oil. In addition the lake often contains stannic oxide in small quantity. The following enumeration of the operations carried out in one of the simpler processes of turkey-red dyeing will give a general idea of the complicated nature of the method.

The cotton (300 kg.) is first freed very completely from fatty and resinous matter by "bowking," or boiling under a pressure of 2 atmospheres with caustic soda solution of sp. gr. 1.005 for four or five hours (p. 521). It is then treated successively three times with turkey-red oil and dried at 70°-75° C. after each treatment. The baths employed for this purpose are "standing" baths, and are freshened up as follows: The first oiling bath is freshened up with 22 kg. acid oil, 5 kg. ammonia, and 22 l. of potassium carbonate solution of sp. gr. 1.26, temperature 40°-45° C. (For a fresh bath two and a half times these quantities are needed.) Second oiling bath like the first; the third oiling bath is freshened up with 20 kg. acid oil and 44 l. potash solutions. After drying, the cotton is now steeped for eight hours in water of 30°-35° C., hydro-extracted and again stoved at 70°-75° C. It is now ready for the alum mordanting bath, which is freshened up with 50 kg. aluminium sulphate, 4.25 soda crystals, the same amount of chalk, and 1 kg. of tannic acid. The cotton remains in this bath for fifteen to twenty hours, is well rinsed and then passed wet into the dye bath. The latter contains about 20 kg. alizarin, 300 g. tannic acid, and about 1 kg. chalk. The material is first treated in the cold bath for an hour; the latter is then slowly heated to boiling, and afterwards boiled first for three hours at 1½ atmospheres pressure with a solution containing 3-4 kg. of soda, then rinsing and finally boiling at 1½ atmospheres with 8 kg. soap, ½ kg. soda, and 400 g. of tin crystals (stannous chloride). It is then rinsed and dried in the air.



Alizarin is also dyed on cotton with chromium mordants for claret red and maroon shades, and on iron mordants for very fast violets.

Wool is dyed with alizarin on aluminium, chromium, iron, and tin mordants; red, maroon, violet, and orange shades respectively are thus produced. The mordants are applied as previously described.

In conjunction with the aluminium mordant 10 lbs. of 20 per cent. alizarin paste, 2 lbs. of calcium acetate, 1 lb. of soap, and  $\frac{1}{2}$  lb. of tannic acid may be employed per 100 lbs. of wool. The latter is introduced into the cold bath, which is then heated to boiling and kept so for an hour and a half. The mordant and the dye are sometimes dyed simultaneously from the same bath where only light shades are required (single bath method).

Silk may also be dyed with alizarin on aluminium, chromium, and iron mordants. About 20 per cent. of alizarin is required for a full shade.

**Other Mordant Dyes.**—The following are the names of some of the dyes which are dyed with mordants and are often termed alizarin dyes, although they are by no means all of them derivatives of alizarin: Alizarin bordeaux, Alizarin maroon, Alizarin orange, Resoflavin, Alizarin yellow, Galloflavin, Anthracene brown, Alizarin green, Emeraldol, Anthraquinone green, Coerulein, Alizarin blue, Brilliant alizarin blue, Alizarin indigo blue, Alizarin sky blue, Cyananthrol, Anthraquinone blue, Gallocyanine, Gallazine, Phenocyanine, Crumpsall fast blue, Alizarin cyanine, Alizarin cyclamin, Alizarin heliotrope, Anthraquinone violet, Anthracene violet, Alizarin black (see pp. 451-454).

In wool dyeing the order of operations is often inverted, *i.e.*, the wool is first treated ("stuffed") with the dye and then saddened with the mordant. This procedure is particularly suitable for a class of dyes of a strongly acid nature known as **acid chrome colours** which have recently been placed on the market. In this case both operations are carried out in the same vessel (single bath process). The dye is first practically exhausted from the bath, and then  $\frac{1}{2}$ -2 per cent. of bichromate, according to the depth of shade, is added and dyeing continued at the boil for half an hour to one hour longer, after which the wool is washed and dried. Chromium fluoride may be employed instead of bichromate with those dyestuffs which will not resist the oxidising action of the latter. The following are names under which this class of dyestuff is sold by various makers: **Chrome, Acid anthracene, Acid alizarin, Diamond salicine**, etc.

**After-treatment of Cotton with Metallic Salts.**—Before leaving the subject of mordant dyes reference must be made to the after-treatment with metallic salts of cotton dyed with the direct and sulphur dyes (p. 545). These salts no doubt act as mordants, although in some cases an oxidising effect exerted by them may also be of importance. Copper sulphate, chromium fluoride, and potassium bichromate are the most important substances employed for this purpose. The following prescriptions will illustrate the process:—

Rinse the cotton well and treat with a cold or tepid solution of 2-4 per cent. of copper sulphate (on the weight of the cotton) for fifteen to thirty minutes; or else with a solution containing 2 per cent.  $\text{CuSO}_4$ , 2 per cent. bichromate, and 3 per cent. acetic acid of 30 per cent. strength under the same conditions; or else boil for half an hour in a bath containing 3-4 per cent. chromium fluoride and 2-3 per cent. acetic acid of 30 per cent. strength.

## VAT DYES

Many dyestuffs are converted by reducing agents (*i.e.*, compounds capable of producing nascent hydrogen or removing oxygen) into colourless substances termed leuco compounds, which by oxidation in contact with air pass again into the original dyes. Some dyes, on the other hand, undergo so far-reaching decomposition when subjected to reduction that a simple process of oxidation cannot reproduce the original compounds. The leuco compounds are frequently soluble in alkaline liquids, and are taken up readily from these by vegetable as well as by animal fibres. On contact with the air the original dyestuff is reproduced in the fibre in an exceedingly fast form. These facts are made use of in dyeing with certain insoluble dyes known as vat dyes. The dye is brought into solution in the vat, *i.e.*, an alkaline



liquid containing a reducing agent. The material to be dyed is impregnated with the leuco-compound formed, and is then exposed to the air, the dye being thus produced in it.

**Indigo.**—This, the most important vat dye, which may be considered to be the parent substance of most of the others in common use, is at the present day employed as natural and as artificial indigo. The former is obtained by a process of fermentation (steeping), followed by one of oxidation (beating) from the leaves of various tropical plants. A glucoside which has been named indican by its discoverer, Schunck, is thus decomposed, yielding glucose and the leuco compound indigo white, which latter is converted into indigo by oxidation. Natural indigo usually contains quantities of the pure dyestuff indigotin, varying between 30 and 70 per cent. according to the source from which it has been obtained; in addition, there may be in it quantities varying between 2 and 10 per cent. of the purple dyestuff indirubin, while the remainder is made up of more or less inert impurities.

The glucoside indican is also contained in woad, a substance that is still employed as an addition to the fermentation vats used in wool dyeing.

Artificial indigo is manufactured chemically from the products of coal-tar distillation. It is met with in commerce as a powder consisting of almost pure indigotin, as a paste containing about 20 per cent. of the same substance, and in various other forms. It is also sold as "indigo vat," a substance containing about 60 per cent. of the leuco compound indigo white (see p. 458).

As already explained the indigo vat contains essentially a reducing agent and an alkaline substance which dissolves the indigo white formed. The latter is either lime, soda, or ammonia, the former may consist of a large variety of substances. Brief reference shall here be made to the hydrosulphite vats, the zinc and lime vat, the copperas vat, and the fermentation vats.

The sodium hydrosulphite employed in the first-named vats is either prepared by the dyer himself by the action of zinc dust on sodium hydrogen sulphite, or it may be obtained commercially at the present day in the form of a dry powder. Either soda, lime, or ammonia may be employed as the alkali of the vat. The vats are usually worked cold for cotton, and at a temperature of about 50° for wool. In the latter case the amount of hydrosulphite is greater, and the amount of alkali smaller, than in the former. A stock or standard vat is always prepared apart from the actual dyeing vat.

The following may be taken as an example of a hydrosulphite-soda vat for cotton, prepared from zinc and sodium bisulphite. Volume of dye vat, 1,000 l. A solution is prepared by mixing 15 l. o. bisulphite solution (sp. gr. 1.28) in small portions with 1.5 kg. zinc dust and letting the mixture stand for a short time with occasional stirring until the sediment is pale grey in colour. A suspension of 15 kg. of 20 per cent. indigo pure paste (equivalent to about 5 kg. very finely ground natural indigo) in about 15 l. of caustic soda solution (sp. gr. 1.38) is then prepared and the first liquid added to the second. The mixture is then maintained at a temperature of about 50° C. during half an hour to an hour. When reduction is complete the stock liquor will have turned yellow. The dye vat (1,000 l.) is prepared with a mixture of 10 l. bisulphite (sp. gr. 1.28) and 1 kg. zinc dust added as above in small portions with stirring. After a short time as much stock liquor as necessary (according to the depth of shade desired) is added and the vat stirred well. It is ready for use as soon as it has become clear and yellowish green. The vat may be used continuously and fed with stock liquor and bisulphite-zinc-soda mixture to keep it up to strength.

For wool a corresponding hydrosulphite-lime vat may be made up by using, in the place of the quantities given above, the following: For the stock liquors 12 l. bisulphite solution, 1½ kg. zinc dust, 10 kg. indigo paste, 10 l. 20 per cent. milk of lime prepared by slaking 2 kg. quicklime in place of the soda solution; for the dye vat, ¾ l. bisulphite solution, 0.2 kg. zinc dust. As already mentioned, the wool is dyed at about 50°, and after dyeing must be passed through very dilute sulphuric acid solution (0.1 per cent.) to remove the lime and then be rinsed.

The following may be taken as an example of a vat for cotton in which commercial sodium hydrosulphite is employed.

The volume of the dye vat is 1,000 l. A stock liquor is prepared by stirring together well 10 kg. 20 per cent. indigo paste (equivalent to about 3½ kg. very finely ground natural indigo), 20 l. cold water, and 1½ kg. hydrosulphite powder. To this, after ten minutes, is added 6 l. caustic soda solution (sp. gr. 1.39), and the whole is heated to 60° C. until reduction is complete. This is



ascertained by dipping a piece of glass into the liquor. The glass and the drops from it should be clear yellow in colour, and the liquor should oxidise in about half a minute. The dye vat is set with 50 g. hydrosulphite to remove dissolved oxygen from the water, and after stirring, the whole or part of the stock solution is added and the vat stirred up once more.

For **wool**, the quantities for the stock solution are 10 kg. indigo paste, 10 l. cold water, 2 kg. hydrosulphite powder, and 2 l. caustic soda solution (sp. gr. 1.38). It is recommended to make the dye vat up with 50 g. hydrosulphite, about  $\frac{1}{2}$  l. ammonia, and  $3\frac{1}{2}$  l. of a 10 per cent. glue solution per 1,000 l. and then to add a portion of the above stock liquor. Dyeing takes place at about 50° C. The vat is used continuously and made up to strength from time to time.

**The Zinc-Lime Vat.**—In this vat, which is extensively used for cotton, the indigo is reduced by nascent hydrogen produced by the action of zinc dust upon a lime solution. It is best to prepare a stock solution of reduced indigo.

The following prescription may serve as an example for the preparation of a vat of 1,000 l. A stock solution is prepared by mixing 10 kg. 20 per cent. indigo paste (equivalent to about  $3\frac{1}{2}$  natural indigo) with  $1\frac{1}{2}$  kg. zinc dust made into a paste with 20 l. of water of 50°-60° C. To this is added 4.5 kg. quicklime which has been previously slaked to a uniform paste. The mixture is made up with hot water to 80 l., and maintained for three to five hours at a temperature of 50°-60° C., with occasional stirring. It should then be pure yellow and ready for use. The vat is set with 250 g. zinc dust and 1 kg. lime slaked to a thin cream, stirred up and allowed to stand for some time. The stock liquor or part of it is then poured in, the vat stirred and allowed to settle. It is then ready for use. A certain amount of sediment is formed; this may trap a small amount of indigo, producing loss, and may also lead to uneven dyeing if proper attention is not paid. These disadvantages, however, are only slight with this vat, being much less serious than in the following one.

**The Copperas Vat.**—This is one of the oldest vats employed in the dyeing of cotton. The ingredients used are lime and ferrous sulphate. Ferrous hydroxide is thus produced which is converted into ferric hydroxide by the indigo contained in the vat, and thus acts as a reducing agent.

The following prescription for a vat of 1,000 l. of medium strength will illustrate the process. A stock vat of 200 l. containing 10 kg. 20 per cent. indigo paste,  $12\frac{1}{2}$  kg. quicklime, and 10 kg. green copperas is made up, and allowed to stand for four to six hours with occasional stirring. As soon as it has assumed a yellow colour, it is poured into the dye vat which has been about three-quarters filled with water. The latter is stirred up and dyeing commenced after it has settled completely. This vat is easy to set, but the large sediment referred to above is a grave disadvantage, and makes it unsuitable for continuous dyeing.

**Fermentation Vats for Wool.**—In the fermentation vats various organic substances are allowed to ferment. Glucose is thus produced which acts as a reducing agent upon the indigo contained in the alkaline liquor. The sugar is oxidised by the latter, first to lactic and then to butyric acid. A great deal of practical experience is necessary to work a fermentation vat properly, and all that can be attempted here is to give a very rough sketch of the most important fermentation vat for wool, *i.e.*, the woad vat.

A vat containing 15,000 l. is often employed. It is filled with water and heated to 65° C., 500 kg. of woad are introduced, and after stirring left overnight. The next morning 20 kg. very finely ground indigo, 20 kg. bran, 7 kg. madder, and 12 kg. lime are added. The whole is stirred two or three times a day with the addition of 1-2 kg. of lime each time, the temperature being maintained at about 60°. After a few days the liquor should show a yellowish colour, and on gently stirring it, blue streaks should make their appearance along with a coppery scum or flurry. Before dyeing, the wool must be very thoroughly scoured and the soap removed. A trammel net is employed in the vat to preserve the wool from contact with the sediment. After dyeing, the wool is thoroughly cleansed with soap and fuller's earth in order to remove all the loosely adhering indigo, which would otherwise show the objectionable property of rubbing when in use.

**Silk** is not very frequently dyed with indigo. The vats must be kept less strongly alkaline than for cotton and are worked in the cold. In applying the various vats, the material is always worked in the liquor for various periods of time—for cotton yarn, three or four minutes; for calico, ten to thirty minutes; and for heavy woollen cloth half an hour to two hours or more. On coming out of the dye vats the goods, which show a greenish yellow colour, are squeezed or wrung and then exposed to the air. The shade quickly passes by oxidation through green to



blue. The operation is then repeated either in a stronger or weaker vat until the desired shade has been attained.

Numerous machines for dyeing with indigo, some of which have been referred to in the chapter on appliances for dyeing, have been designed for use with the various forms of textile goods. They are designed to carry out the operations of steeping and oxidising the goods in a continuous manner.

**Other Vat Dyes.**—During the last 30 years a considerable number of new vat dyes have been put on the market, most of which are distinguished by their great fastness to light and other influences, and which promise to become of the very greatest importance in the future. They are mostly employed in conjunction with the hydrosulphite vats. The following are the more important classes:—

**The Thioindigo Class** is of great theoretical interest. They are chemically derived from indigo by replacing NH groups by S atoms. The following are some of the more important dyes of this series: Thioindigo red, Thioindigo scarlet, Thioindigo violet (Kalle), Vat red B (B.A.S.F.), Helindone red 3B, Helindone orange R, Helindone yellow 3G, Helindone scarlet S, Helindone fast scarlet, and Helindone brown G (M.L.B.). All these dyes may be employed for cotton and wool (see p. 463).

**The Ciba Colours** (S.C.I.B.) are apparently either brominated indigo derivatives or derivatives of the thioindigo class. Most of them may be applied equally well to animal and vegetable fibres. The more important ones are various indigos put on the market by M.L.B. and the B.A.S.F. Ciba blue B and 2B (S.C.I.B.), Ciba heliotrope, Ciba Bordeaux B, Ciba red G, Ciba scarlet G, Ciba grey G and B, Ciba green G, and Ciba violets (see pp. 461, 466).

**The Indanthrene, Alcole (B.A.S.F.) and Leucole (Bayer) and Cibanone (S.C.I.B.)** colours have no chemical connection with indigo, but are mostly related to anthraquinone. They require the addition of a large amount of alkali to the hydrosulphite vat, and are therefore unsuited for use with the animal fibres. The following may be mentioned: Indanthrene yellows (flavanthrene), orange, copper, reds, Rufanthrene browns (fascanthrene), Indanthrene claret, Indanthrene blues, Indanthrene violets (violanthrene), Indanthrene grey, Indanthrene maroon (olivanthrene), Indanthrene brown, Indanthrene green (viridanthrene), Indanthrene blacks (melanthrene), Alcole yellows, orange, scarlet, reds, grey, blues, pink, green, Bordeaux, Cibanone yellow, orange, browns, and blacks (see p. 454).

Certain of the sulphide dyes, such as kryogene black, may also be dyed in the vat, and should, therefore, be mentioned here (see pp. 458, 478).

## DYESTUFFS PRODUCED BY CHEMICAL MEANS ON THE FIBRE

### Aniline Black

This dyestuff, which is of the greatest importance in cotton dyeing, is always produced on the fibre as a perfectly insoluble substance by the oxidation of an aniline salt. When an acid solution of aniline is treated with suitable oxidisers, the base undergoes a very complicated series of oxidations and polymerisations, a considerable number of intermediate products is produced and ultimately a black insoluble substance of very high molecular weight "aniline black," is formed (p. 480).

This substance appears to exist in two states of oxidation or polymerisation: the first has the property of acquiring a greenish tint under the action of sulphurous acid, the second more highly oxidised, or perhaps only more highly polymerised product does not exhibit this reaction; and it is this form which the dyer must aim at producing, if the dyed fabric is not to turn green during use. The cotton is, therefore, usually subjected to an after-treatment in a hot chrome bath in order to convert



the whole of the first into the second form of aniline black. The oxidiser employed for oxidising the aniline salt in the first instance may be sodium (or potassium) chromate; potassium ferricyanide (red prussiate of potash), or what comes to the same thing, a mixture of sodium chlorate and potassium ferrocyanide; or lastly, sodium chlorate. The last-named substance requires the intervention of a catalyst or carrier of oxygen, and as such, a salt of copper, iron, or vanadium may be employed. The same substances are sometimes also added to chromate solutions to accelerate oxidation. The oxidation takes place in the fibre, with a suitable velocity at temperatures at or about  $45^{\circ}\text{C}$ ., and the following processes, producing what are termed (1) dyed blacks, (2) aged blacks, and (3) steam blacks, are in use. In the first-named process the material (say 100 kg.) is worked in a dye bath of 2,000 l. containing, say, 13 kg. aniline salt, 20 kg. hydrochloric acid (sp. gr. 1.171), 14 kg. bichromate, first in the cold for an hour. The temperature of the bath is then raised to  $70^{\circ}\text{--}80^{\circ}\text{C}$ . and the cotton is worked for another half hour, during which the black is developed. It is then rinsed and soaped well, hydro-extracted, and dried. The disadvantage of this process is that the dyestuff is not held well by the fibre and rubs badly. The second or **ageing process** is the one most frequently employed. It differs from the first in making use of a much more concentrated solution, and in the fact that the oxidation is not accomplished in the liquor itself, but that the fabric is removed from it, dried, and then aged, that is, subjected to a moist warm atmosphere which develops the black. During the process of ageing large quantities of hydrochloric acid and oxides of chlorine are liberated from the aniline hydrochloride, and there is thus always a considerable risk of tendering the fabric if the temperature is not carefully regulated and the acid efficiently removed by the current of air. An addition of aluminium acetate is recommended to neutralise the mineral acid given off.

The following prescription for yarn by K. Oehler will give an idea of the process. The cotton is first thoroughly boiled out with soda, well rinsed, hydro-extracted, and stretched. 25 kg. are then turned for half an hour in a padding liquor made up to 500 l., after pouring together the following solutions: 60 kg. aniline salt dissolved in 320 l., 2.75 kg. bluestone (copper sulphate) dissolved in 50 l., 18.8 kg. sodium chlorate dissolved in 37 l., 2 kg. ammonium chloride dissolved in 12 l., and 18 l. of an aluminium acetate solution (sp. gr. 1.075). The yarn is then wrung or hydro-extracted lightly until it retains about its own weight of liquor. It is then well stretched, placed on wooden laths which have been wiped over with the padding liquor, dried, and aged. The drying and ageing are conveniently carried out in the same chamber; the drying takes about four to six hours, the ageing proper is begun by carefully admitting steam until the dry bulb thermometer registers  $35^{\circ}\text{C}$ ., the wet bulb  $30^{\circ}\text{C}$ . The ageing chamber is fitted with a powerful fan at the top, which draws in air through the bottom; this air is heated by means of pipes which also serve for the introduction of steam. While in the ager the yarn is turned every two hours; the ageing occupies about six to eight hours. After leaving the ager the yarn is chromed by turning quickly for ten to fifteen minutes at  $75^{\circ}\text{--}80^{\circ}\text{C}$ . in a bath containing 3 kg. bichromate and 0.75 kg. sulphuric acid per 1,000 l. It is then thoroughly rinsed, soaped, rinsed again, and dried.

A process which bids fair to become of the very greatest importance in the production of aged blacks has been recently patented by A. G. Green. In it the only oxidising agent employed is atmospheric air. This is accomplished by making use of the observation that a small quantity of a diamine, *e.g.*, paraphenylenediamine, constitutes, when associated with a copper salt, a catalytic system by means of which aniline can be readily oxidised by air alone.

In the **Steamed Blacks** the oxidising substance is essentially potassium ferricyanide. The cotton may be padded with a liquor containing 75 kg. aniline salt, 35 kg. sodium chlorate, 40 kg. yellow prussiate of potash per 1,000 litres; it is then dried at a temperature not exceeding  $50^{\circ}\text{C}$ ., and the black then developed by steam in a few minutes in a suitable ager.

The advantage of this process over the ageing method lies in its rapidity and in the fact that there is little risk of tendering, as very little mineral acid is given off in the presence of the potassium ferrocyanide; its disadvantage lies in the greater expense.

Various other bases besides aniline may be oxidised on the fibre to produce aniline blacks or other dyes. Thus a black is obtained from *p*-amidodiphenylamine and a brown from *p*-phenylenediamine.



## Ice Colour (see pp. 442, 450, 545)

The ice colours are employed in cotton dyeing. They belong to the class of insoluble azo dyes, and are produced on the fibre itself (p. 545) by the same chemical processes by means of which azo dyes are manufactured in the colour works.

As is well known (see p. 441), the following operations are carried out in the production of azo dyes: First an aromatic base is diazotised by dissolving it in an excess of acid, cooling the solution with ice, and adding to it a solution of sodium nitrite. As soon as the starch iodide test shows that the nitrous acid is no longer being used up in the chemical reaction, the diazotised solution is poured into an alkaline solution of a phenol, or it is allowed to act on a slightly acid, neutral, or alkaline solution of an aromatic base (see pp. 442, 450).

In the production of azo colours in the cotton fibre, the latter is always impregnated first with the alkaline solution of the phenol.  $\beta$ -naphthol is the substance almost exclusively employed for this purpose. The cotton is padded in small quantities at a time in a strong solution containing the naphthol and caustic soda and some turkey-red oil. The material is then hydro-extracted and dried quickly in a well-ventilated room at medium temperature. After it has been thoroughly well cooled it is ready to be developed by introducing it into the solution of the diazotised base. Various substances producing different shades, viz., diazotised paranitraniline, chloranisidine, alphanaphthylamine, and other diazo bodies are in use for this purpose, but the first-named is the easiest to work and the most frequently employed. The dye obtained is known under the name of paranitraniline red. The diazotisation is in this case carried out by pouring together the very carefully weighed out chemicals, and should take place at a low temperature (say  $10^{\circ}\text{C}$ ). The temperature should never rise higher than about  $15^{\circ}$ . Since a strongly acid solution, like the one obtained in this operation, will not couple with a phenol, it becomes necessary to make it either neutral or feebly acid by the addition of caustic soda or sodium acetate respectively. The solution must not be made alkaline since diazo solutions are unstable in this condition.

It is thus obvious that great care must be taken by the dyer in weighing out his chemicals. As a rule, his weighings alone are relied upon to give the right proportions, and are not checked by special tests. Compared with other diazo salts, those derived from *p*-nitraniline are exceptionally stable, and it is a great advantage to the dyer that these diazo-salts may be obtained commercially, ready made. They are sold mixed with indifferent substances, such as aluminium or sodium sulphate, to render them non-explosive, and are found on the market under the names of Nitrazol C (Cassella) and Azophore red (M.L.B.). Another product of a similar nature is nitrosamine red (B.A.S.F.) which represents *p*-nitrophenylnitrosamine sodium (antidiazotising *p*-nitrobenzene sodium). This substance is converted into *p*-nitrodiazobenzene chloride by simply adding hydrochloric acid in the cold to its solution. It is then allowed to stand for half an hour, and on the addition of sodium acetate it is ready to be employed in the process of developing.

In conjunction with the ice colours the two processes known respectively as "diazotising and developing" and as "coupling" must be considered here. Both processes are employed extensively as methods of after-treatment for the direct cotton colours. The last-named is also applied occasionally to cotton, dyed with the sulphur colours.

The majority of direct cotton colours belong to the class of amido bodies, some to the class of phenols. The former may be subjected to both methods of after-treatment under consideration, the latter only to the second. In the first-named process the dye is diazotised on the fibre, and the compound formed, coupled with the solution of a suitable developer, *i.e.*, either an amido body or a phenol. In the second process the dyed fabric is treated directly with the solution of a diazotised base, or of one of the commercial diazo bodies mentioned above.

The following prescriptions will illustrate the methods:—

**Diazotising and Developing.**—Wash the material well after dyeing with the direct cotton colour and then work for fifteen to thirty minutes cold in a dye bath charged with 1-3 per cent. sodium nitrite and 5-10 per cent. spirits of salt (hydrochloric acid). The cotton is lightly rinsed and passed without delay or unnecessary exposure to light and air into the cold developing bath in which it is worked for fifteen to thirty minutes. It is then washed and dried. Of the numerous developers



which may be employed, the following may be mentioned: Phenol, Resorcinol, Alpha and Beta Naphthol, Para-aminodiphenylamine, etc. The first four are dissolved in caustic soda, the last named in the minimum amount of hydrochloric acid.

Prescription for "coupling" for 100 kg. cotton: Make 0.5-0.6 kg. of paranitraniline into a paste with an equal quantity of hot water, then add 1-1½ l. of cold water and 1.5 kg. hydrochloric acid (sp. gr. 1.16) and let stand until the mixture has cooled to 20° C. Then stir in 2 kg. broken ice and add all at once ½ kg. solid sodium nitrite, taking care that the temperature does not rise above 10° C. Pour this solution into the coupling bath which has been filled with cold water, and add a solution of 1½ kg. crystallised sodium acetate. Enter the dyed and rinsed cotton, work for about thirty minutes, rinse, and dry.

## Mineral Colours

Although largely displaced by modern organic dyes, yet a few mineral colours have still retained a certain degree of importance in cotton dyeing. They are always produced in the fibre itself as insoluble pigments from substances which are not dyes.

**Chrome Yellow and Orange.**—These substances consist of ordinary and basic lead chromates respectively (see p. 500). Chrome yellow may be produced by fixing lead oxide on the fibres, and then passing it through a hot dilute solution of potassium dichromate. The first-named operation is carried out by impregnating the material with a soluble lead salt, and then passing it through dilute lime water. Another method of procedure consists in impregnating the cotton first with an alkaline lead solution containing, say, 1½ per cent. lead acetate and 0.8 per cent. caustic soda (on the water), and then passing through an acidified solution of bichromate containing, say, 1 per cent. of bichromate and ½ per cent. sulphuric acid.

Chrome orange is obtained by dyeing the cotton first with chrome yellow, washing, and then working in boiling clear dilute lime water until the desired shade has been obtained.

**Manganese Brown** is obtained by impregnating cotton with a solution of manganous chloride, and then passing it through a hot solution of caustic soda (sp. gr. 1.01) free from carbonate. Colourless manganous hydroxide is thus precipitated, which is converted into the brown higher oxides of manganese by exposure to air and a passage through a weak solution of bleaching powder.

**Mineral Khaki** may be obtained by impregnating the cotton with a mixture of ferrous and chromic acetates. After drying, it is then steamed in a rapid ager which leads to the production of a mixture of basic ferric and chromic acetates on the fibre. These are further fixed by passing the goods through a boiling solution containing a mixture of sodium carbonate and sodium hydroxide.

**Iron Buff** consists of ferric hydroxide, and may be dyed on cotton by the same method employed for manganese brown, only substituting green vitriol for manganous chloride. It may also be obtained by successive treatment with a ferric salt and caustic soda or lime.

**Prussian Blue** may be obtained on cotton by first dyeing it an iron buff, and then working it in cold solution of potassium ferrocyanide containing, say, 2 per cent. ferrocyanide, 1 per cent. sulphuric acid, on volume of bath (see p. 502). Prussian blue is frequently employed as a groundwork in the dyeing of heavy blacks on silk.

Prussian blue is also dyed on wool. It is usually obtained by the oxidation at a high temperature of hydroferro or hydroferri cyanic acid liberated respectively from potassium ferro, or potassium ferri cyanide. An addition of a stannous mordant improves the colour.

The wool may be introduced into a cold bath containing 10 per cent. red prussiate of potash and

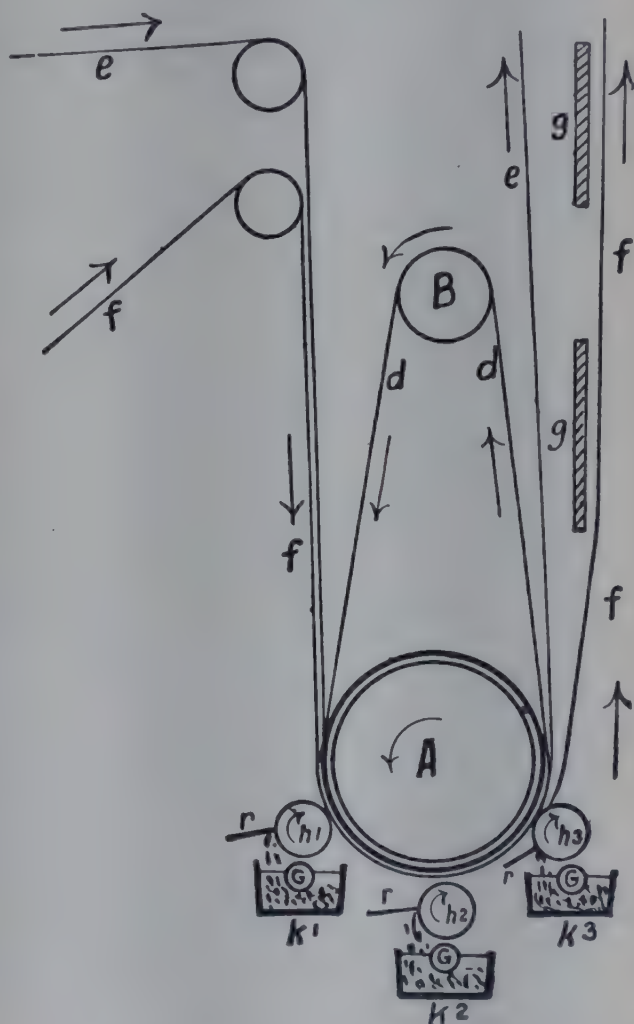


FIG. 223.—Section of Three-Colour Printing Machine.



20 per cent. sulphuric acid (on weight of wool). The temperature is gradually raised to boiling and maintained thus for about half an hour or more. About 1-2 per cent. of stannous chloride may be added towards the end of the operation.

## COLOUR PRINTING OF CALICO

In colour printing the dyes are confined to certain portions of the fabric, being printed on by special rollers and prevented from spreading to neighbouring parts by the addition of thickening agents to the dye, such as starch paste, dextrine, gum arabic, gum tragacanth, albumen, casein, and similar substances. The dyes are usually applied in a water-soluble form, as in dyeing, and are fixed in the fibres by

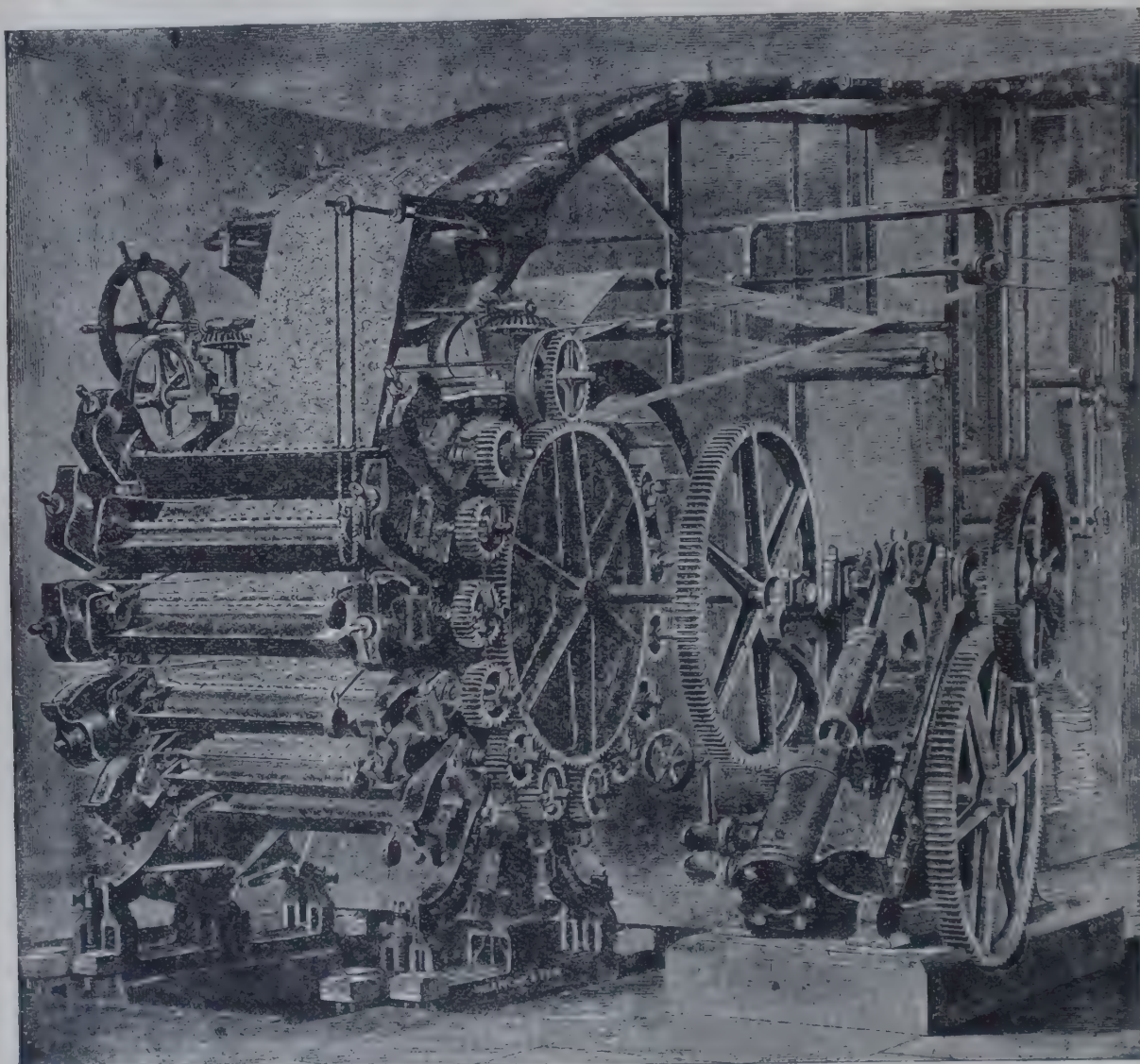


FIG. 224.—Twelve-Colour Printing Machine. (Mather & Platt.)

suitable mordants followed by steaming in chambers. Sometimes insoluble colouring matters are fixed on with adhesives—usually blood albumen (see p. 597); on steaming the albumen coagulates and fixes the dye in an insoluble wash-fast form on the fibre. Such colours are known as “albumen colours,” and comprise insoluble mineral colouring matters, such as ultramarine, Guignet’s green, chrome yellow, cinnabar, zinc white, etc.

The printing is carried out by means of hollow copper rollers, usually  $1-1\frac{1}{2}$  yds. long by 4-6 in. in diameter, provided with a steel core. The patterns are etched on the copper by means of acid in the usual way, the colour collecting in the hollows of the roller and being pressed on to the cloth as it passes under it. Each colour has its own roller with its own special pattern. Printing machines are now made in which one to fourteen colours are printed on the cloth in a single operation, usually



on one side only of the fabric, but in duplex machines the patterns, exactly corresponding, are printed on both sides.

Fig. 223 shows the principle of a printing machine (three-colour). A is a large hollow iron roller a yard or more in diameter, covered with a thin layer of cloth; over this and over a smaller roller B runs the endless rubber cloth *d*; over this runs the cloth *f* which is to be printed, together with a supporting cloth *e*; *h*<sub>1</sub>, *h*<sub>2</sub>, *h*<sub>3</sub> are the printing rollers, which take up colours from the rotating rollers placed in the colour cisterns *k*<sub>1</sub>, *k*<sub>2</sub>, *k*<sub>3</sub>; any excess of colour is scraped off the printing rollers by the special knife edges *r*, *r*, *r* pressing against them. The cloth *f* as it passes between each printing roll and the large iron cylinder has a coloured pattern printed on it. The cloth then passes away and is immediately dried (to prevent the colours from running) by passing over hot plates *g*, *g*, or into a hot drying chamber. The colours are then fixed by steaming in a special chamber.

## THE DYEING OF SYNTHETIC FIBRES

This section deals with the dyeing of viscose, acetate, cuprammonium, and other synthetic fibres.

The acetate rayon dyes which were first brought into use about twenty-five years ago are now used not only for rayon but for nylon, saran, vinyon, P.V.C., polythene, and many other new plastics (see also under Plastics). The so-called acetate dyes are oil soluble. Typical examples are **Sudan red**, **Oil black GN** (Geigy), and **Nigrosine**. These materials have little application in the dyeing of textile materials such as cotton, but in the case of acetate rayon and other plastics dyeing takes place by actual solution in the material of the fibres.

When acetate rayon dyes were discovered, dyers judged the value of the dyes they used by their solubility in water. The acetate rayon dyes are practically insoluble in water. Consequently, somewhat different techniques are required during their use.

In dyeing with normal water soluble dyes, those dyes are preferred which possess the greatest water solubility. Dye manufacturers assist water solubility by introducing groups such as (COOH), (OH), (NH<sub>2</sub>), or (SOOH). Another part of normal dyeing technique is to add common salt to the dye solution by degrees as the latter becomes weaker. This tends to reduce the solubility of the dye in water and produces in effect a stronger concentration of dye where it is required, namely at the surface of the fibres.

When the above technique was applied to acetate rayon it was found that the greater the solubility of the dye in water the smaller was its affinity for acetate rayon. Nearly all the acid wool dyes and the direct cotton dyes were found to be useless for colouring acetate rayon. It soon became well known that when the dye contained a solubilising group such as those given above, it would very likely be useless for dyeing acetate rayon. As water is considered the most convenient medium for dyeing, a means was required of introducing the oil soluble acetate rayon dyes into water. This was effected by means of dispersing agents such as soap, Turkey-red oil, or one of the synthetic dispersing agents. (See Martin and Cooke, "Modern Soap and Detergent Industry.") It should be noted that these oil soluble acetate rayon dyes do not possess water solubilising groups and are fairly readily absorbed from water suspension by acetate rayon. Thus the dyeing of acetate rayon requires a rather modified technique. In cotton and wool dyeing the dyestuff is absorbed by the fibres and held between them by chemical forces. In the case of acetate rayon dyeing the dye is dissolved by the acetate and is held in solution by physical forces. When a cross-section of a dyed acetate rayon fibre is microscopically examined, it is found that the dye has penetrated uniformly throughout the fibre, whereas in the case of dyed cotton, silk, or wool it is found that the dye is only absorbed by the surface of the fibres—the dye particles are too large to pass into the centre of the fibres.

Deep shades are fairly easily produced in the dyeing of acetate rayon owing to the high solvent power of acetate rayon towards the oil soluble dyes.

The above remarks apply equally to nylon and most other thermoplastics



where it is found that the acetate rayon dyes are by far the best. In several of the newer plastics, however, it is found that the solubility of the acetate rayon dyes is less than in acetate rayon itself. In these cases it has been difficult to obtain deep shades. In the case of polyvinyl chloride the Geigy Company have brought out a useful series of water soluble dyes which can be used to dye the polymer before plasticising. These dyes are very fast and produce shades that are deep enough for cable identification purposes.

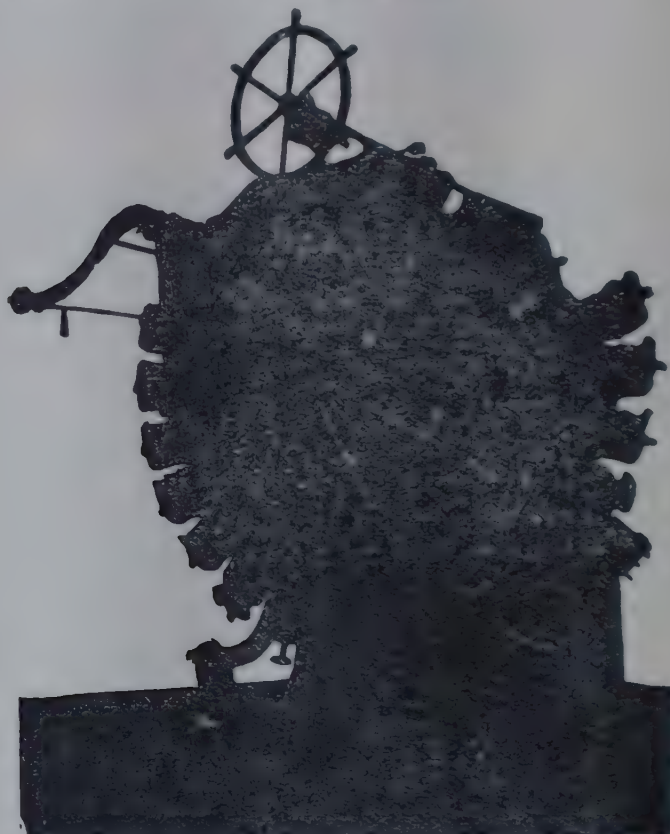


FIG. 225.—Fourteen-Colour Printing Machine.  
(Mather & Platt.)

Although direct cotton dyes and acid wool dyes have not been found satisfactory for the dyeing of acetate rayon, the increasing use of spun rayon in sportswear has focused attention on the application of fast colours to this class of material. The vat dyes, leuco-esters of vat dyes, and naphthols are expected to maintain the excellent reputation for fastness to light and washing that they have earned when used for cottons. In the case of acetate rayon the vat colours may be applied by the pigment pad-jig development, pigment pad-reel development, reel dyeing, continuous reduced method, and pigment pad-continuous methods. For more detailed information on this very interesting but lengthy subject the reader is referred to the literature at the beginning of this section.

## FINISHING

### LITERATURE

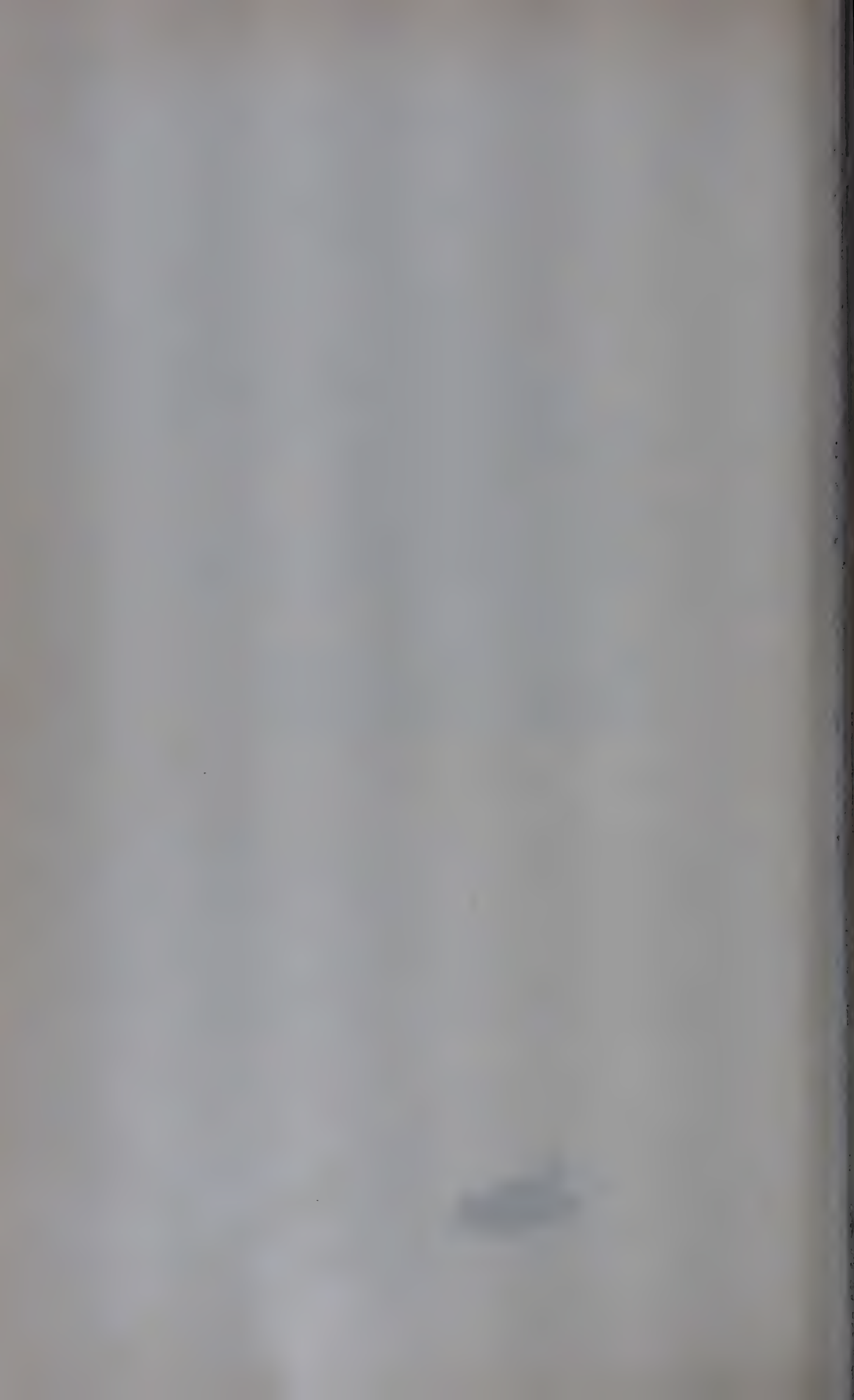
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The printed cotton cloth is always "finished" in order to weigh it and give it a better appearance. The finishing materials consist of starch paste ("size"), mixed with such mineral salts as kaolin, gypsum, barium sulphate, magnesium sulphate, chalk, etc. If a highly glazed surface is required a little paraffin or soap is added. To obtain a pure white, and correct any yellowish tinge, it is usual to mix in ultramarine or other suitable colouring matter in small amount. A "soft" touch is imparted to the cloth by the presence of magnesium chloride, calcium chloride, or glycerol, which are all hygroscopic. The finishing paste is evenly spread over the cloth by means of "sizing" machines, and dried by passing the cloth over hot drums. Shrinkage is avoided by drying in a stretched condition in special frames. The goods are then "calendered" by passing between hot smooth steel rollers, whereby they acquire a fine glaze. A fine silky appearance may be given to cotton goods by stamping or subjecting to very great pressure between special rolls (satin). Woollen goods (*e.g.*, flannel) may be given a rough hairy appearance by passing over rotating cylinders provided with fine steel points. **Cloth** is made by mechanically working woollen goods in soap solution, whereby the fibres become more or less matted together ("milling" or "fulling"). For particulars of this and other special processes works on cloth-making must be consulted.

**Acknowledgments.**—The author wishes to express his thanks to the following firms who supplied him with many samples of dyed material and with much information regarding the newest processes of dyeing: Read Holliday & Sons, Ltd.; Cassella & Co.; The Badische Aniline u. Soda Fabrik; Meister Lucius & Brüning; Kalle & Co.; Farbenfabrik F. Bayer & Co.

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## SECTION XIX

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### The Leather and Tanning Industry





# THE LEATHER & TANNING INDUSTRY

Originally written by D. J. LAW, B.Sc., F.R.I.C.

Revised by E. I. COOKE, M.A.(Cantab.), B.Sc., A.R.I.C.

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IN the following pages the writer has endeavoured to give, as far as possible, a review of the processes through which the raw hide or skin passes during its conversion into leather. From the exigencies of space it is evident that the merest outline only can be given of some of the more typical methods, since no two factories follow exactly the same method of procedure, and the possible modifications of the standard processes are endless.

A short account of analytical processes is given in those cases only in which they differ from, or are not included in, the ordinary methods of quantitative analysis.

The writer wishes to acknowledge the help received from information contained in Professor Procter’s “Principles of Leather Manufacture,” also his thanks to Mr J. T. Wood for reading the proofs.

The illustrations are from blocks kindly supplied by Messrs T. Haley & Co., Bramley, Leeds.

The magnitude of the leather industry may be gauged by the following statistics:—

### IMPORTED INTO THE UNITED KINGDOM.

	1906.	1910.	Value in 1910.
Undressed-leather - - - -	925,252 cwt.	904,205 cwt.	£5,051,827
Dressed leather - - - -	360,144 „	271,366 „	4,336,677
Varnished, japanned, or enamelled leather	6,541 „	7,095 „	241,167
Leather machinery belting - - -	4,457 „	3,069 „	38,297
Leather boots and shoes - - -	211,501 doz. pairs	168,236 doz. pairs	673,674
Leather gloves - - - -	1,513,888 „	1,367,498 „	1,561,753
Other manufactured leather goods - -	...	...	595,020
Dry raw hides - - - -	484,218 cwt.	516,896 cwt.	1,855,804
Wet raw hides - - - -	533,678 „	764,155 „	2,417,028
Total - - - -	...	...	£16,771,247

## EXPORTED FROM THE UNITED KINGDOM.

	1910.	Value.
Undressed leather - - - - -	105,373 cwt.	£885,848
Dressed leather - - - - -	113,919 "	1,892,570
Varnished, japanned, or enamelled leather -	1,262 "	36,223
Leather machinery belting - - - - -	39,448 "	515,450
Leather boots - - - - -	1,080,638 doz. pairs	3,029,822
Leather gloves - - - - -	228,870 "	342,110
Other manufactured leather goods - - - - -	...	527,887
Raw hides - - - - -	196,962 cwt.	552,021
Total - - - - -	...	£7,784,209

The following statistics refer to the United States :—

## IMPORTED INTO THE UNITED STATES.

	1910.	Value in 1910.
Patent, japanned, or varnished leather - -	1,230 cwt.	\$237,000
Skins for morocco - - - - -	...	1,941,000
Upper, dressed and finished - - - - -	...	972,000
Calf skins, tanned - - - - -	...	270,000
Chamois and other - - - - -	...	1,356,000
All other - - - - -	...	2,779,000
Manufactured leather, gloves - - - - -	...	7,782,000
Manufactured leather, all other - - - - -	...	1,476,000
Hides (cattle, goat, sheep, etc.) - - - -	5,434,000 cwt.	112,247,000

## EXPORTED FROM THE UNITED STATES.

	1910.	Value in 1910.
Sole leather - - - - -	342,200 cwt.	\$8,308,000
Upper leather - - - - -	...	15,988,000
Manufactured leather—		
Boots and shoes - - - - -	7,257,000 pairs.	12,400,000
Harness and saddles - - - - -	...	842,000
All other - - - - -	...	1,082,000
Hides and skins - - - - -	130,700 cwt.	1,738,000

For modern statistics see Appendix III.

(For Tanning Materials see p. 575.)

The object of leather manufacture, as defined by Professor Procter, is the conversion of the "putrescible animal skin into a material which is permanent and not readily subject to decay, while retaining sufficient softness and flexibility for the purposes for which it is intended."

## Theory of the Tanning Processes

The nature of the change which the raw hide undergoes during the process of its conversion into leather is not well understood. The issue is complicated by the fact that the raw materials (including the gelatinous hide fibre, the vegetable tannins,



and the basic mineral salts used in tanning) are "colloidal," and follow the laws of colloidal chemistry, a branch of the science neglected till very recently, but in the investigation of which great strides have been made during late years. The main point at issue is whether the process is to be looked upon as a chemical combination between gelatine and tannin, or a mutual co-precipitation of colloids.

Sir Humphry Davy\* in 1803 precipitated solutions of gelatine by tannin and found that the quantity of precipitate produced is not always exactly proportional to the amount of gelatine and tannin in the solutions used, but is influenced by the concentration of the solutions. J. T. Wood,† working on similar lines, considers the precipitation neither purely chemical since the gelatine-tannin compound is not of constant composition, nor purely physical since the precipitation does not obey the solution laws, which require the concentration of the tannin in the solution and in the precipitate to maintain a constant ratio. The physical theory was first proposed by Knapp in 1858, who was also the first to recognise the fact that the conversion of skin into leather consisted of the drying of the fibres without allowing them to adhere. Stiasny‡ thinks that the hide first adsorbs the tannin from its colloidal solution, and then the tannin undergoes a further change under the catalytic action of the hide fibre. He explains the increase of insoluble matter which goes on after the leather is tanned as due to further chemical changes in which oxidation plays a large part. Fabron, from the result of a large number of experiments in chamois, aldehyde, vegetable and mineral tannages, thinks that leather consists of a salt of the oxidised hide fibre.§ Though holding that the true tanning process is purely chemical, he recognises that the simultaneous physical processes of capillarity, diffusion, and adsorption are indispensable. He points out|| that the inner parts of the hide are accessible to crystalloids only and differentiates between true tannages in which the condensation takes place directly between the tanning agent and the hide fibre, and pseudo-tannages in which the tanning agent undergoes some change before acting as such.

Dr J. von Schroeder¶ considers tanning primarily an adsorption process, and that the adsorption compound undergoes a change in the course of time, resulting in a more stable union of the tannin with the hide fibre. He finds that tannin is not taken up by hide powder from alcoholic solution, and from this emphasises the importance of the action of water in swelling the fibre and thus rendering it in a condition to be precipitated by tannin. The final solution of the problem will probably lie in regarding the process as the effect of both chemical and physical forces acting in conjunction.

### The Raw Skin

The structure of the skin of all the mammalia is essentially the same though differing greatly in thickness and texture according to its origin. So far as leather-making is concerned skin may be taken as consisting of two layers, the outer constituting the **epidermis** or **epithelium** (E, Fig. 226), and the inner the **corium** or **dermis** (C), the true skin.

The epidermis, which is completely removed in the operations of liming, etc., before tanning, is very thin in comparison with the true skin. Its inner surface consists of a mucous layer, the "*rete malpighi*," which is in contact with the corium and is made up of soft cells, of which the wall is composed of keratin. These cells in the living organism are continually being forced toward the outer surface, their place being taken by new ones. As they approach the surface they become flattened and finally dry, and forming a horny layer, drop off. The epidermis is thus in a continual state of renewal. Separating the epidermis from the corium is the **hyaline layer**. This constitutes the extremely thin "grain" surface of the tanned leather and is of a different structure from the rest of the corium, which is apparent from the different colour of the leather in any place from which it has been removed before tanning. The hair (H, Fig. 226) and sweat (S) and fat-glands (T) are developed from the epidermal layer, and the hair in the early stages of its growth grows backwards into the corium, whence it derives its nourishment.

The structure of the **corium** or true skin differs essentially from that of the epidermis, and consists of bundles of interlacing fibres which are themselves composed of fibrils of extreme fineness cemented together by a somewhat more soluble substance. The texture is looser in the centre of the skin, especially so in sheep skins of which the grain and flesh may frequently be torn apart. The structure becomes much more compact at the surface just below the epidermis and constitutes the *pons papillaris* or "grain" and contains the fat-glands. The appearance of this surface and the arrangement of the hair-openings is frequently the only evidence from which the origin of the skin, after tanning, can be deduced. The **dermis** also contains fibres of another character termed the "elastic fibres,"

\* *Phil. Trans.*, 1803, 233.

† *Journ. Soc. Chem. Ind.*, 1908, 384.

‡ *Zeitsch. f. Chemie und Industrie der Kolloide*, 1908, vol. 9.

§ *Zeit. für Angew. Chemie*, 1909, 2083-97, 2135-44, 2187-94.

|| *Collegium*, 1910, 240-259.

¶ "Zur Kenntniss des Gerbprozesses" (*Kolloidchemischen Beiheften*), 1909.



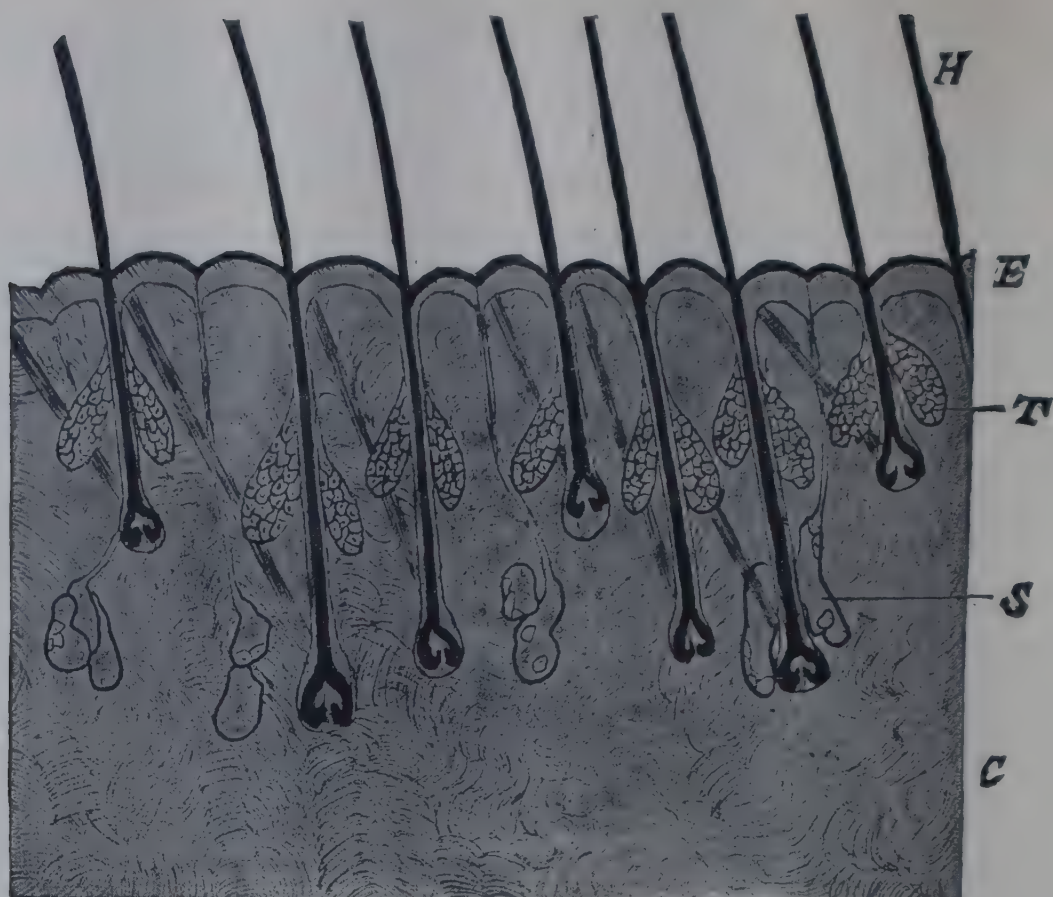


FIG. 226.—Vertical Section through Skin.

these are yellow in colour and differ greatly from the rest of the skin substance in their resistance to dilute acid, which causes the fibres of the connective tissue to swell and become transparent while the yellow fibres are unaffected.

The chemical composition of the white connective tissue corresponds very closely to that of gelatine into which it is converted by boiling with water. Von Schroeder and Paessler give the following figures for the ultimate analysis of purified corium: C 50.2 per cent., H 6.4 per cent., N 17.8 per cent., and O 25.4 per cent.

An important property of gelatine or hide fibre, from the tanner's point of view, is its capacity of combining both with acids and bases, which it does by virtue of the amido and carboxyl groups contained in the molecule. Under the action of dilute alkalis or acids, or by heating under pressure, gelatine is converted into peptones which do not gelatinise on cooling but resemble gelatine in being precipitated by tannin and meta-phosphoric acid. Longer periods of such treatment or raising to higher temperatures result in the final splitting up of the molecule into nitrogen, ammonia, water, and carbonic acid, with amido acids as intermediate products. Similar products are the result of the action upon gelatine of gastric and pancreatic juice and enzymes secreted during the growth of bacteria. The interfibrillar substance of the raw hide consists of corium which differs from the connective tissue in some respects, notably in its greater susceptibility to solution by dilute solutions of caustic alkali. Procter, however, considers it probably merely an impure degradation product of hide fibre or gelatine.

The epidermis, hair, and glands belong, chemically, to the class of "Keratins." They are more readily attacked by caustic alkalis than is the gelatigenous hide fibre, hence the use of lime for the removal of hair and epidermis. They also differ from gelatine in not swelling in cold water, only dissolving in hot water at temperatures above  $100^{\circ}\text{C}$ .

The raw material for the manufacture of leather may be taken as consisting of three classes—hides, kips, and skins.

**Hides** consist of the skins of oxen, cows, and horses. In addition to the fresh market hides of home origin, sun-dried hides are imported from the Argentine, Uruguay, China, and Africa, and from America, Europe, and the Colonies in the salted condition.



**Kips** are the skins of small native cattle, imported mostly from India either in the dried or dry-salted condition, or after a rough and incomplete native tannage.

For the manufacture of the lighter kinds of leather the major part of the raw material consists of the **skins** of calves, sheep, and goats. Skins of deer, pigs, and seals are also used to some extent. The skins of snakes, alligators, and some fish yield a leather which is much used in the manufacture of fancy articles. Much leather is made in Australia from the skins of the kangaroo, wallaby, and other marsupials. Hippopotamus, elephant, and walrus hides are tanned into a very stiff and thick leather used in the "buffing" of cutlery.

**Water.**—In an industry such as we are dealing with in which such large quantities of water are used, the quality of the water supply is of extreme importance. The presence of a large amount of lime and magnesia compounds results in a great loss of tannin, which is rendered inactive through the formation of an insoluble precipitate. Even in cases where no combination takes place the presence of dissolved salts in water used for leaching tanning materials materially reduces its efficiency.

Eitner \* has studied the effect of water, containing various salts in solution, on the raw hide. In his experiments the hide had been unhaird by sweating, and was kept in contact with the solutions for four days at a temperature of 46° F. Water containing lime sulphate and magnesia sulphate had the greatest plumping effect, while the carbonates of lime and magnesia present in the same strength produced a moderate plumping. The chlorides of magnesia and sodium had a repressing action, as hide in these solutions was less plumped than in distilled water. He also found that hide was well plumped in water saturated with CO<sub>2</sub>. These results, being obtained with the use of sweated hide, will naturally not hold in the case of a limed hide. Thus a limed hide brought into water containing carbonic acid or bicarbonates will "full" on account of neutralisation of the lime. The precipitation of calcium carbonate in this manner is frequently a source of trouble, as scudding is thereby rendered difficult and the knife is liable to break the grain. The weak acids in the bates and puers will remove lime but not the calcium carbonate, which is dissolved by the drench acids, leaving the skin, however, permanently damaged in those portions in which the "blasting" has occurred.

Iron is especially objectionable if present to any appreciable extent in the water used for preparing goods for tanning, its presence resulting in a bad colour by combination with tannin. Decaying organic matter and the presence of bacteria are objectionable, and a frequent source of danger in the soaks. Where the hardness of the water supply is such as to render its use impossible, one of several methods of softening are employed.

**Soaking.**—The treatment undergone by the hides or skins previous to entering the limes is modified by the state of the goods or the method of preservation used. Hides which have been preserved by the use of salt require more washing than fresh ones, in order, as far as possible, to remove the salt which would otherwise hinder satisfactory plumping in the limes. Dried hides and skins require a comparatively long soaking before the requisite degree of plumpness and flexibility is attained, while with fresh market hides the object of soaking is simply the mechanical removal of blood and dirt.

The use of putrid soaks was formerly much resorted to, but is largely superseded owing to the loss of hide substance thereby incurred, and the danger of destruction of the goods by excessive bacterial action. Softening and cleansing is much hastened by drumming in the tumbler (Fig. 227), through which a stream of water is kept running as the drum revolves. A more violent softening treatment is that of working in the "faller-stocks" (Fig. 228) in which the goods are placed in a wooden or metal box in which two heavy hammers, actuated by pins on the circumference of a revolving wheel, fall alternately.

Mechanical treatment has been rendered unnecessary to a large extent by the addition of various swelling agents in small quantities to the soak water. Solutions of caustic soda (1 : 1,000) or sodium sulphide (1½-3 : 1,000) as suggested by Eitner

\* Gerber, iii., 1877, p. 183.



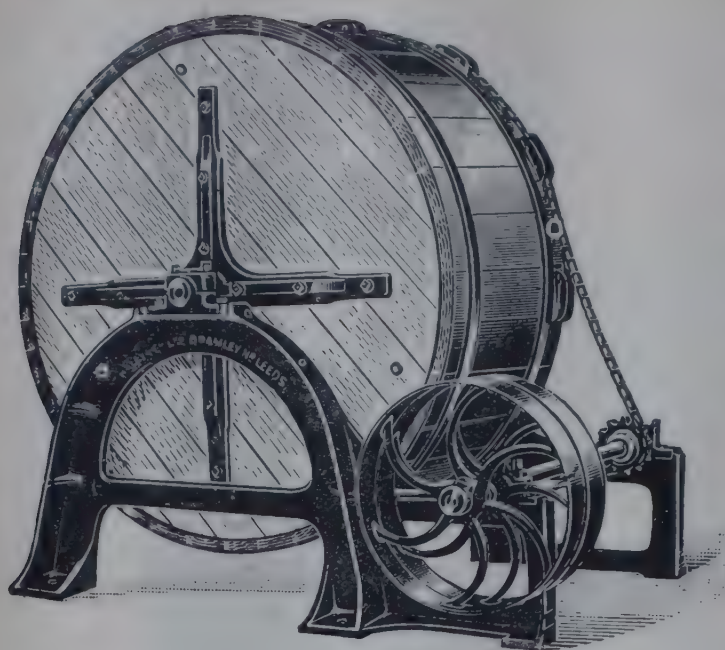


FIG. 227.—Tumbler.

are the most commonly used, swelling being rapidly obtained, and all danger of putrefaction being avoided. Solutions of sulphurous acid and dilute mineral acids are also used.

The process of soaking largely determines the ease with which subsequent processes in leather manufacture can be carried out. This point is especially relevant to the process of liming where a quicker and easier process results.

Fresh skins are too often neglected, but they often contain substances such as blood and interfibrillary proteins which are better removed. The same remarks apply, of course, to salted skins which, in addition, are often

partially dehydrated and must be properly wetted back. There are also dry salted skins and sun dried skins which must also be properly wetted back in addition to the removal of protein and dirt.

The use of wetting agents such as the sulphated fatty alcohols has in the view of at least one school of thought been over-emphasised. They are stated to be of little value except in the case of skins that are very greasy. The scientific approach to wetting and rehydration is to make use of the natural tendency of proteins to swell in acids and alkalis. In the case of acids, the swelling is quick and difficult to control, but with alkalis the correct degree of swelling can easily be attained. Alkalis such as ammonia, sodium hydroxide, and sodium sulphide are generally used.

The two main methods used for removing interfibrillary proteins are the common salt method and the ammonia or alkylamine method. The latter are very useful in that they have a certain solubilising action upon the interfibrillary proteins, giving a soft stretchy leather.

When using sodium sulphide or polysulphide for soaking it is important that drying should be complete. Otherwise the anaerobic bacteria often present become very active in the presence of these reducing agents and cause considerable loss of pelt.

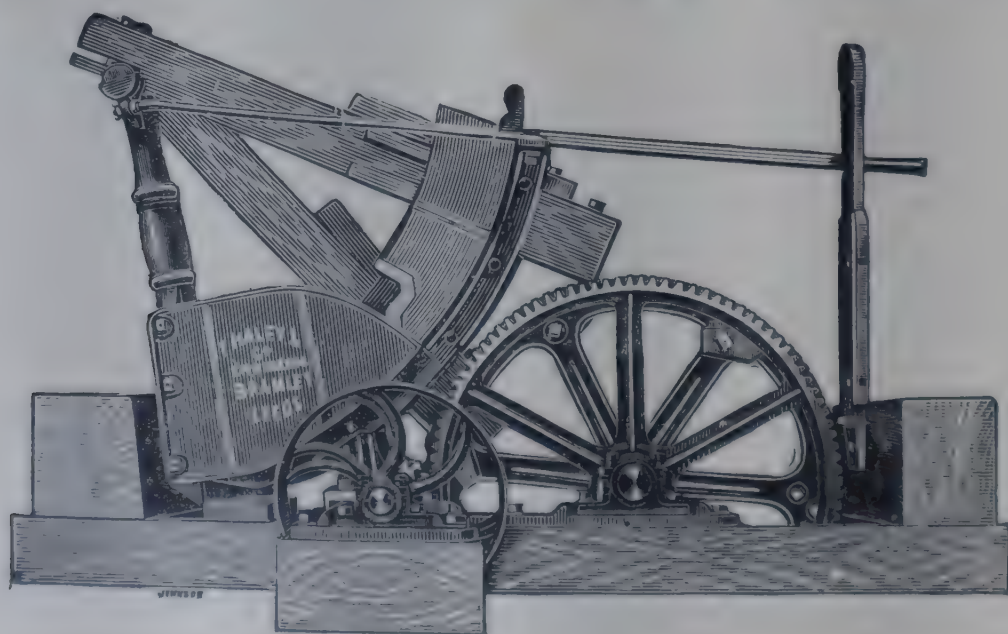


FIG. 228.—Faller-Stocks.



Three typical soaks might be as follows:—

(a)	Sodium hypochlorite	-	-	1 part.
	Water	-	-	1,000 parts.
(b)	.880 ammonia	-	-	0.2 parts.
	Water	-	-	1,000 parts.
(c)	25 per cent. diphenylamine solution	-	-	1.0 parts.
	Water	-	-	1,000 parts.

It should be mentioned that the soak (a) is designed for the dual purpose of providing weak alkalinity and for providing an oxidising bactericidal solution. This prevents to a large extent the action of the anaerobic bacteria.

When large quantities of interfibrillary protein are to be removed, soaks (b) and (c) are best used. When a bactericide is required for these soaks an oxidising type such as sodium trichlorophenoxide at a concentration of 1 part in 10,000 is used. When there are quantities of blood present 5 per cent. of common salt is used in the liquor.

### Depilation

A method of depilation which was practised more generally in earlier times and still to a considerable extent is that by means of "sweating." The hides or skins are hung in a closed chamber in a damp atmosphere and with little or no ventilation. Ammonia is produced in large quantities by bacterial action on the hair roots, and the hair or wool is quickly loosened.

There is always danger of damage to the grain by excessive bacterial action, and the process finds its principal application in the removal of wool from sheep skins where the wool removed is more valuable than the skin. It is also used for the removal of hair from hides for sole leather, but the process was never a success in England, probably on account of bad management. Goods which have been sweated must be brought into a swollen condition before tanning—this is done either by a subsequent treatment with lime or by acid in the earlier liquors.

The general method of unhairing is by the use of lime. This step in the manufacture of leather is the one which has undergone least modification in the light of increasing scientific knowledge.

The reason for this probably lies in the exceeding safeness of the process. The limited solubility of lime (a saturated solution is of about one-twentieth normal strength) imposes a limit on the strength of the alkaline solution, and the tanner can, and always does, use a large excess of lime. The slowness of its action, also, permits of the proper duration in time of liming to be greatly exceeded without material damage to the goods. The removal of hair, although the most apparent of the effects of the liming process, is only one of the results attained by it. The hide substance, as shown above, consists of an agglomeration of fibres which are themselves capable of being split up into bundles of exceedingly fine fibrils. This is actually brought about in a fully limed skin, which, on that account, offers an enormously increased surface to the tanning liquor which coats each fibre with an insoluble and isolating covering. Solution of the interfibrillar substance also takes place in the lime liquors, which are regulated according to the class of goods for which the skin is intended. Thus, this solution of hide substance is reduced to a minimum in the case of hides for sole leather, while, with light skins, in which suppleness and softness are aimed at in the finished article, it is encouraged and carried further in the puer-shop. In the case of skins to be tanned with chrome, which is, in itself, an "empty" tannage, solution of interfibrillar matter is kept at a minimum.

Lime is received at the tanyard in the form of quicklime,  $\text{CaO}$ , and requires to be slaked before use.

The presence of magnesia,  $\text{MgO}$ , is objectionable, as it causes the "slaking" process to be extremely slow, and may result in the damage of the goods by burning holes in them.

The method, and also the duration, of liming varies greatly in different yards, and also for different classes of goods in the same yard. Von Schroeder recommends the proportions of 6 lbs. of lime to 100 gals. of water. 6 per cent. of lime on the weight of the hides is known to be sufficient; many tanners, however, use 10–15 per cent. on the weight of the hides.



The two main systems of liming are the old French system and one in which the hides are taken right through the process in one pit. In the old French system the goods pass through three pits containing respectively an old, medium, and new lime. The new pit, after having one pack of goods through, becomes a "medium" lime, and the medium, in the same way, an old, while an old lime is run away after having the one pack of goods through. In the one-pit system the liquor is strengthened up from time to time by running away part and adding fresh milk of lime. The hides are simply laid horizontally one by one in the milk of lime and drawn out ("hailed") and replaced ("set") once, or even twice a day. Skins are frequently limed in paddles, and systems are in use in which the hides are suspended vertically in a pit in which the liquor is kept in movement by an agitator near the bottom of the pit. A method, used largely in America for sole leather, known as the Buffalo method, consists in treating the hides with lime for a short time, frequently with the addition of sulphides, followed by warm water, by means of which they are quickly in a condition for uphairing. Messrs Payne and Pullman\* have patented a method by means of which lime is precipitated in the interior of the hide with a great saving of time and capability of modification according to the requirements of the goods. This is accomplished by treating the goods first in a 2 per cent. caustic soda solution, followed by a  $1\frac{1}{2}$  per cent. solution of calcium chloride. The previous treatment of the goods in a putrid soak liquor is necessary if the hair is to be removed, as the process does not accomplish this without the aid of bacterial action.

The time necessary for thorough liming varies with different classes of goods; hides are usually given from seven to ten days while sheep skins require a longer time.

The time of liming is greatly shortened by the addition of various substances which "sharpen" the lime. Sodium sulphide to the extent of  $\frac{1}{4}$ – $\frac{1}{2}$  per cent. on the weight of the hides is a very common addition which loosens the hair very rapidly, and lessens the solution of hide substance. Alkaline carbonates accelerate the liming action by increasing the alkalinity of the solution. Red arsenic sulphide and calcium sulphhydrate are also used. Sheep skins, from which the wool must be removed with as little damage as possible, are treated on the flesh side with a paste of lime and sodium sulphide, and laid in pile, and after a few hours the hair is pulled off without having come in contact with the alkali.

The hair is removed by working with a blunt knife (Fig. 229) over a sloping convex beam of wood with a zinc covering, and the hides are placed in water as soon as possible after that operation in order to prevent carbonation of the lime through contact with the air. It is often difficult to remove the short under hair which is more deeply rooted than the rest; this can often only be effected by shaving with a sharp knife.

There are several machines in use for the removal of hair; in the Leidgen machine, one of the most commonly in use, a cylinder fitted with blunt knives revolves against the surface of the hide which is kept in contact with it by the pressure of a rubber apron. The hides are also fleshed after the liming process. This is done with a heavy two-handled knife (Fig. 229) over a beam similar to the unhairing beam. The knife differs from the unhairing knife in having both its edges sharp, and the action is partly scraping and partly a cutting one; the mechanical action of the knife in forcing out fat, etc., is also important. Manual labour has, in this process also, been partly superseded by machines of which the Jones and the Vaughan fleshing machines are the most important.

In modern depilation technique sodium sulphide is most commonly used nowadays. A still more recent variation of this technique is to use sodium hydrogen sulphide in place of sodium sulphide. When this is done it is easier to control the alkalinity of the solution and also the sodium ion concentration. In this way the degree of swelling of the skin is controlled, giving a very fine grain leather. The sodium hydrogen sulphide can be used in equivalent proportions to sodium sulphide and made up into a paste with lime in a similar way for painting on to the back of the skin. Nowadays, however, the use of lime, especially for valuable skins, is tending to go out of favour. The reason for this is that depilation takes place by the breakdown of the cystine group of the keratin, and this is accelerated by the presence of a reducing agent such as sodium hydrogen sulphide. When using the latter it is thus not necessary to use lime as a thickener, especially in view of the dangers of using lime with wool. If a thickener is required for the depilatory paint a neutral substance such as China clay has been suggested with the addition of a little ammonia to give the necessary hydroxyl ion concentration. The above points are, of course, of most interest when the wool from a skin is required as well as the skin.

\* English Patent, 2,873, 1898.



After the wool has been removed liming of the skin is probably the most important process. It determines the quality of the leather. The days of long liming are over and it is recognised that a short liming is suitable for any kind of leather provided that the composition of the liquor is varied to suit the leather. In the past it was common to find limings taking up to twenty days.

The theory of liming has been fairly fully explained. A brief summary is given here.

When a fibre is removed from a skin, immersed in lime water, and examined over a period of days, it is found that water permeates between the fibrils in the fibre bundle, causing the bundle as a whole to swell without the fibrils swelling. After a further period of time the fibrils themselves begin to swell. It appeared that for proper liming the first part of this swelling only was required. Further work showed that the addition of ammonia or amines to the first liming liquor caused rapid swelling of the fibre bundle without rapid swelling of the fibrils. This is similar to the old mellow lime technique but the method has the advantage that pelt substance losses are low. The synthetic "mellow lime" is also much more speedy, resulting in an initial liming of only eight hours. When using this method the second liming comprises a straight lime with increased causticity, obtained by means of sodium hydroxide. After this stage of the liming the fibrils have swelled, thus completing the liming in a total of only sixteen hours compared with up to twenty *days* by the old method. Use of this technique has resulted in stronger and better skins as the loss of hide substance due to hydrolysis is so much less.

As an example of a modern liming treatment the following formula is given:—

First bath.	.880 ammonia	•	•	0.2 per cent.
	Hydrated lime	•	•	2.0 „ „
Second bath.	Soda ash	•	•	0.3 „ „
	Hydrated lime	•	•	3.0 „ „

After the liming process is completed, excess calcium oxide must be removed. Ammonium chloride is by far the best deliming agent. About 2 per cent. is used in the deliming drum. It has been suggested that the process as at present practised requires too long and that it could be speeded up by the use of a more concentrated solution of ammonium chloride retaining, however, the same quantity of ammonium chloride calculated on the weight of skins. It has also been suggested that the time of deliming could be considerably shortened by raising the temperature of the solution to blood heat. For example:

Drum the skins in only 70 per cent. of the usual quantity of water containing a quantity of ammonium chloride calculated on the number of skins and their calcium oxide content. Raise the temperature to 38° C. and maintain this temperature until the skins and liquor are at the same pH. Then dilute the water in the drums until at 200 per cent. concentration (maintaining the temperature at 38° C.). When the pH of the skins has again reached equilibrium with that of the liquor the latter is run off and washing begun in the usual way.

The use of small quantities of hydrochloric acid to speed the action of the ammonium chloride has also been suggested.

**Chemical Control of the Lime Yard.**—The alkalinity of a lime liquor increases with its age owing to the formation of amines and ammonia as the final products of the splitting up amino acids derived from the hide substance. The alkalinity of a lime liquor in which lime alone has been used therefore affords a very good indication of its age. (A saturated solution of CaO at the ordinary temperature has an alkalinity of about 4.7 c.c.  $\frac{N}{10}$  HCl per 10 c.c.)

**Dissolved hide substance** is determined by the usual Kjeldahl method after evaporating with a little dilute sulphuric acid. The percentage of nitrogen multiplied by 5.62 will represent the amount of dissolved hide substance.

A useful test of the amount of hide substance dissolved in a lime liquor has been proposed by Seymour-Jones. 50 c.c. of the filtered liquor is placed in a cylinder and made slightly acid;

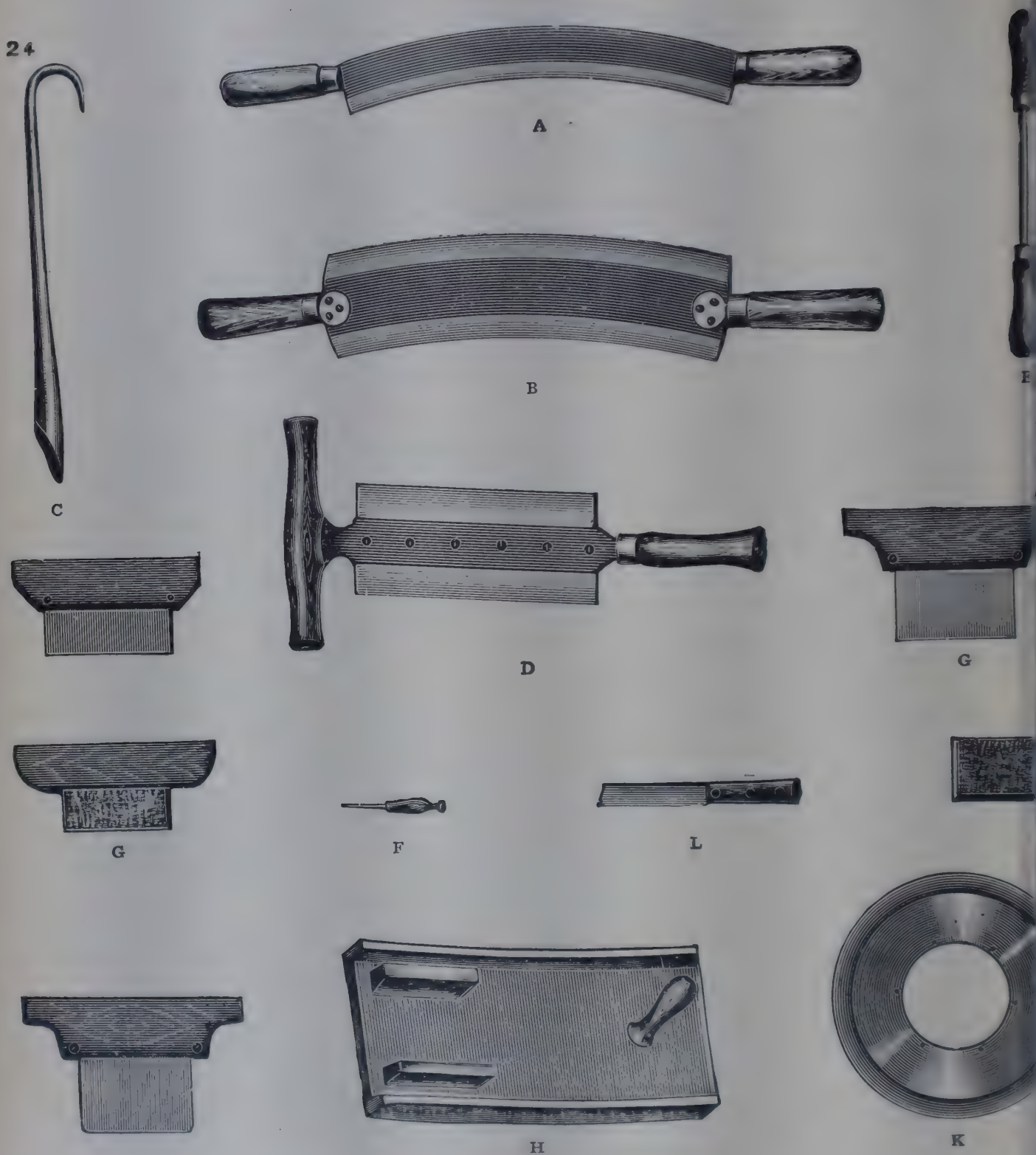


FIG. 229.—Tanners' and Curriers' Tools.

- A. Unhairing Knife
- B. Fleshing Knife
- C. Pit Hook

- D. Shaving Knife  
E, F. Curriers' Steels  
G, G. Slickers

- H. Arm-Board  
K. Moon Knife  
L. Rounding Knife



saturated salt solution is then added to make the volume up to 100 c.c. The greater part of the hide substance is thus precipitated and collects at the surface of the liquid, and by measuring its volume after a definite period of time the test may be made roughly quantitative.

**Ammonia** is determined by boiling the liquor for fifteen to twenty minutes in a flask connected with a condenser, and absorbing the ammonia evolved in a known volume of standard acid which is then titrated back. For improvements see Procter and M'Candlish.\*

**Sulphides** may be estimated by the volumetric method, using zinc sulphate solution.

### Degreasing

Formerly, the normal way of degreasing a skin was to press the grease out of the pickled skin or to dissolve it out by means of paraffin to which was added alcohol or a sulphated fatty alcohol. The latter materials were used to lower the interfacial tension between the wet grease in the skin and the paraffin. The disadvantage in using this method is that the paraffin and the additives used with it possess a high affinity for the skin and are difficult to remove. The above fatty alcohol sulphates are ionic wetting agents. It has recently been found that the non-ionic wetting agents are far better than the ionic in the above application in that they have no affinity for the skins.

Aqueous degreasing has been found to work well in cases where the skins do not contain large quantities of fatty acids. The polyethenoxy group of non-ionic emulsifying agents is used to form an emulsion of water and grease. When, however, the concentration of free fatty acids is too great the emulsifying properties of the above agent become specific and inefficient. Further work is required to ascertain the exact conditions under which the aqueous degreasing technique will work for all concentrations of free fatty acid. Advantages of aqueous degreasing are that it is less trouble, cleaner, the odour of paraffin is avoided, and recovery of the fat is easier. The latter is done simply by heating the emulsion to 45° C., when the fat and emulsifying agent rise to the surface to be collected for soap manufacture (already containing a small quantity of wetting agent which actually improves the action of the soap).

### Filling

It has recently been found that if a very fine dispersion of an inert material such as polyvinyl chloride, of particle size of the order of 0.5  $\mu$  in water, is brought into contact with a skin after liming and washing, the polyvinyl chloride is absorbed by the skin, increasing its weight by 30 per cent. Only twenty minutes is required for this action. The dispersion is stable to electrolytes of pH 1.5 to 12, but the addition of common salt to more than 3 per cent. causes coagulation.

The leather resulting from this technique has more weight, and is for this reason useful for the production of suède. In the heavy leather trade it has been found possible to introduce this polyvinyl chloride emulsion into sole leather after tanning, and even in tanned leather an uptake of between 20 and 25 per cent. is obtained. The absorbed P.V.C. cannot be washed out after absorption, and it is suggested that van der Waals forces prevent this.

The above technique is also being extended to tannins such as quebracho (of high molecular weight). Normally they are introduced into the skin by solubilising by the use of sulphite. This tends to reduce the molecular size of the tannin. The new technique only reduces the particular size which is of the order of 0.5  $\mu$ . This size enables the skin to absorb the tannin very easily. One disadvantage the new method has is that the particular dispersing agent used tends to make the skin too easily wettable due to the hydrophilic nature of the dispersing agent. This, however, is not an insuperable trouble, and the use of

\* *Journ. Soc. Chem. Ind.*, 1906, 254.



a hydrophobic wetting agent which will satisfactorily disperse the tannin should result in the speedy adoption of this method.

### The Vegetable Tanning Materials

The present state of knowledge with regard to the constitution and classification of the tannins is unsatisfactory. In many cases each material contains a different variety of tannin, and the tannin even from the same plant may be of a different constitution as it resides in a different part of the plant (wood, bark, fruit, etc.). A certain broad distinction, however, may be drawn between the tannins according to their reaction with a solution of a ferric salt. Pyrogallol tannins yield a blue-black colour when treated in this manner, while catechol tannins give a greenish black colour. This distinction is, in the main, borne out in their behaviour when used as tanning materials. Catechol tannins also give a precipitate with bromine water which is not the case with pyrogallol tannins.

The constitution of two members of the pyrogallol group has been determined with reasonable certainty. These are gallotannic acid (from gall nuts), which is probably di-gallic acid, and yields gallic acid under the action of dilute acids and some unorganised ferments, and ellagitannic acid (usually present in mixture with gallotannic acid), which yields ellagic acid under the same conditions, and is the source of "bloom" deposited by some tanning materials, notably myrobalans, valonia, and divi-divi. The tannins of the catechol group, on the other hand, yield no gallic acid or bloom on boiling with dilute acids, but generally give a deposit of "reds," which are anhydrides of the tannin and insoluble in water. The lower anhydrides are not completely insoluble, and form the difficultly soluble portions of many tanning materials. They may be brought into solution completely by the use of alkalis or alkali sulphites, which is done to a great extent in the manufacture of soluble quebracho extracts. (See *Inks*, p. 490; and *Dyeing*, p. 548.)

Tannin is usually present to the greatest extent in the bark in the interior of thick-walled cells. The outer dead covering of bark ("ross") in most cases contains very little tannin. The percentage of tannin in wood is usually low, though in many cases its extraction is rendered commercially practicable by the cheapness of the raw material. Insect galls often contain a very high percentage of tannin which is here undoubtedly a morbid secretion of the plant induced by the puncture of the insect.

The following are some of the more important vegetable tanning materials:—

**Algarobilla** consists of the pods of several of the Cæsalpinias, chiefly *C. brevifolia*, a native of Chili. The tannin, being held loosely in the fibre, is very easily extracted. It is one of the strongest tanning materials known. A sample of the pods, freed from seeds, examined by the writer, showed 60.8 per cent. of tannin by the official method.

**Babool**, *Acacia arabica*.—The bark containing 12-20 per cent. tannin is used to a considerable extent in India. The pods, which also contain tannin, are used in India for bating.

**Canaigre**, *Rumex hymenosepalum*, is grown in Mexico and Texas. The tuberous roots contain when dried 25-30 per cent. of a catechol tannin. It is prepared by slicing thinly and drying rapidly, and gives a leather of a bright orange colour.

**Chestnut**, *Castanea vesca*.—The bark contains tannin up to 17 per cent. but is not much used as a tanning material. The wood, containing 3-6 per cent. tannin, is used in great quantity in the manufacture of chestnut extract.

**Divi-divi**, *Cæsalpinia coriaria*.—The tree is a native of Central America. The dried pods contain 40-45 per cent. tannin which is used as a partila substitute for gambier.

**Gambier**, *Nauclea gambir*.—A climbing shrub of the East Indies. The material appears in commerce as cube gambier, a hard earth-like substance containing about 45 per cent. tannin, and as block gambier containing 30-35 per cent. tannin and 35-40 per cent. water. Gambier is extracted from the leaves and twigs of the plant by chopping and boiling with water until the latter becomes



syrupe; the leaves are then removed. The liquid, on cooling, becomes a pasty mass which is cut into cubes and dried either by the heat of the sun or by wood fires.

**Hemlock**, *Abies canadensis*, hemlock fir.—The bark, containing 8-10 per cent. tannin, is used to an enormous extent in America and yields a dark red coloured leather. It is also the source of hemlock extract.

**Larch**, *Larix europea*.—The bark contains 10-12 per cent. tannin and is used to a great extent in the tannage of light leather, principally basils, to which it imparts a fine colour.

**Oak**.—The bark of many species of oak is used as a tanning material and was one of the earliest tanning agents used. The bark, containing about 10 per cent. tannin, is used to a great extent in the manufacture of sole leather, but has been replaced to some extent by extract made from the wood. Oakwood extract is also used for the tannage of sheepskins for roller leather.

**Valonia**, the acorn cups of *Quercus agrifolia* from Asia Minor, contains about 35 per cent. tannin, of which the larger quantity is in the "beard," and is much used in the manufacture of the heavier leathers.

**Galls** containing a large percentage of tannin are abnormal growths on various species of oaks produced by the puncture of insects, principally of the Cynips group. "Knoppeln" are galls produced in the immature acorns of various species of oaks, principally *Q. Cerris*, and were formerly very largely used.

**Myrobalans** are the fruit of *Terminalia chebula*, a tree indigenous to India. They contain 30-40 per cent. tannin but vary a great deal in quality. They are divided into several grades known as "Bombays," "Jubbulpores," and "Vingorlas."

**Quebracho**, *Loxopterygium Lorenzii*.—The wood of the tree, grown principally in the Argentine, contains about 20 per cent. of a red difficultly soluble tannin. It is now used to an enormous extent in the form of extract, made, for the most part, in the quebracho forests. The greater part of the extracts are made completely soluble by the use of alkalis or sulphites.

**Sumac**, *Rhus coriaria*.—A shrub grown in great quantities in Sicily and Italy. The leaves and shoots are gathered, and after drying are finely ground, and as such the material appears usually in commerce. The ground sumac is "ventilated" or winnowed to remove sand and small particles of iron. It is divided into two grades, "mascolino," the best, which should contain 27-30 per cent. tannin, and "feminella" consisting of the inferior grades. Sumac is particularly liable to adulteration, principally with the leaves and stems of *Pistacia lentiscus*, the most important work on the detection of which was done by Andreasch.\* Lamb and Harrison† have also published a very satisfactory method of detection of adulterants of sumac by microscopical means.

**Wattle**.—Many species of the genus *Acacia* are used as tanning materials in Australia, and may have a tannin content up to 50 per cent.

**Synthetic Tanning Materials**, or "Syntans," have been produced by E. Stiasny (see *Journ. Soc. Chem. Ind.*, 1913, 32, 775) by heating phenols with formaldehyde in a slightly acid solution and then sulphonating the product to render it soluble. The Badische Co. put it on the market as "Neradol D." See also French Patents, 443,730, 1912; 451,875, 1912; 451,876, 1912; English Patents, 8,511, 1912; 8,512, 1912; 24,216, 1912; 24,982, 1912.

## Extraction of Tanning Materials

The extent to which the preliminary grinding of the material is taken is of importance as it must be sufficient to allow as complete penetration of the water as possible, while avoiding reduction to a powder which would cake when wet, and result in clogging of the leaches. The most general method of extraction of tanning materials in use is the "press-leach" system. The leaches consist either of pits sunk in the earth constructed of brick and cement or wood, or vats or square receptacles above the surface of the ground. A set consists of any number up to twelve. Each is provided with a false bottom consisting of wooden laths on which the tanning material rests, leaving a space underneath to allow the removal of the liquor. All the leaches are connected by means of a pipe or "trunk" passing from the bottom of one into the top of the next right through the series. When in working order the leaches contain material in all stages of extraction, and the liquor from the strongest is run off for use in the pits. As strong liquor is drawn off from the head leach an equal quantity of water is pumped into the weakest, and floating on the top of the liquor in that leach forces some of it into the next, and so on through the whole series. By this means the nearly exhausted material is brought in contact with fresh water with consequent great thoroughness of extraction. Before the

\* "Sicilianischer Sumac und seine Verfälschung," Wien, 1898.

† "Sumac and the Microscopic Detection of its Adulterants," *Journ. Soc. Dyers and Colourists*, March 1899.



material from the first leach is thrown out ("cast") it is finally extracted with hot water by which further quantities of tannin are extracted. The water is heated by blowing in steam or by an arrangement of steam coils below the false bottoms of the leaches, of which systems the latter, though costly, is preferable, as live steam is injurious to the leaches. A better system is that of using the silent-boiling jet, which is also used, as suggested by Professor Procter, to circulate the water in the vat, which results in very complete extraction of the material. The material in the first leach being exhausted, is "cast," and the leach refilled with fresh material. This leach then becomes the head leach of the system, and receives the liquor from what was previously the head leach. In the Holbrook system the liquor is pumped from one pit to another instead of being left to find its level under the action of gravity. Care is taken never to let a leach run dry, as the material would sink down and form a compact mass resulting in incomplete percolation through the formation of channels. Sprinkler leaches were formerly much used in America. The material was placed in round tubs fitted with a revolving pipe above for the delivery of the water. The water was sprayed upon the leach from small holes in the horizontal pipe as it revolved. The extraction with this system was very incomplete, and great loss of tannin was occasioned through oxidation.

Where the liquor is to be used in the manufacture of extract it is decolourised on coming from the leaches. It is mixed with a proportion of blood or albumen and heated to 70° C., at which temperature the albumen coagulates and carries down much of the colouring matter. Evaporation is carried out under reduced pressure in order to decrease loss of tannin by oxidation, which would occur if evaporated at atmospheric pressure. The Varyan triple effect evaporator is greatly used for this purpose. By the use of this system, in which the steam from the weakest liquor is used to heat the second and so on, the liquor will pass through the whole apparatus in four or five minutes, and increase in density from about 1.02 to 1.20 without having been heated above 70° C. The Kestner evaporator is also much used (see pp. 82*a*, 158*a*, 594).

The import of **tanning substances** into the United Kingdom in 1910 is shown in the following table:—

	1910.	Value.
Bark for tanning - . . . . .	560,000 cwt.	£226,000
Extracts for tanning . . . . .	...	749,000
Gambier . . . . .	5,000 tons	155,000
Myrobalans . . . . .	861,000 cwt.	225,000
Sumac . . . . .	11,000 tons	106,000
Valonia . . . . .	18,000 cwt.	169,948
Various . . . . .	21,000 cwt.	12,760

For modern statistics see Appendix III.

### Sole-Leather Tanning

After the unhairing and fleshing process, hides for sole leather are "rounded." This is done with a sharp knife on a table, and enables the tanner to give a cheaper tannage to the inferior portions of the hide. In England the custom is to divide the hide into "butts" or "bends," which constitute the best part of the hide, and "offal," which includes the bellies, shoulders, and cheeks (Fig. 230). In America it is more usual to divide the hide, by a cut down the centre of the back, into "sides." Before the goods enter the tan liquors, some deliming process is necessary, as a brittle grain and bad colour would result if they were tanned in the condition in which they came out of the limes. Formerly, a simple washing in water was considered sufficient, supplemented by the acid in the earlier liquors, but now it is almost universally the custom to use an acid bath for this purpose. It is of great importance that the lime should not be completely removed as an excess of acid would be as injurious as that of alkali. The safest acid used is boric acid, and a great improvement in colour is effected by a treatment of the goods in a 1½-



per cent. solution of this acid. Sulphurous acid is also good, and organic acids, such as lactic, acetic, and formic acids. Sulphuric acid yields good results, but great care is necessary to avoid excess.

The progress of the deliming action is easily followed by moistening the cut edge of the hide with an alcoholic solution of phenolphthalein when any free lime in the hide immediately produces a pink colour.

The object of the sole-leather tanner is to obtain weight, solidity, and waterproofness in his finished goods.

In earlier times this was accomplished by leaving the goods in comparatively weak liquors for a great length of time, the actual tanning process often taking from twelve to eighteen months, but the introduction of extracts and the consequent facility of producing much stronger liquors has, in most cases, shortened this time considerably.

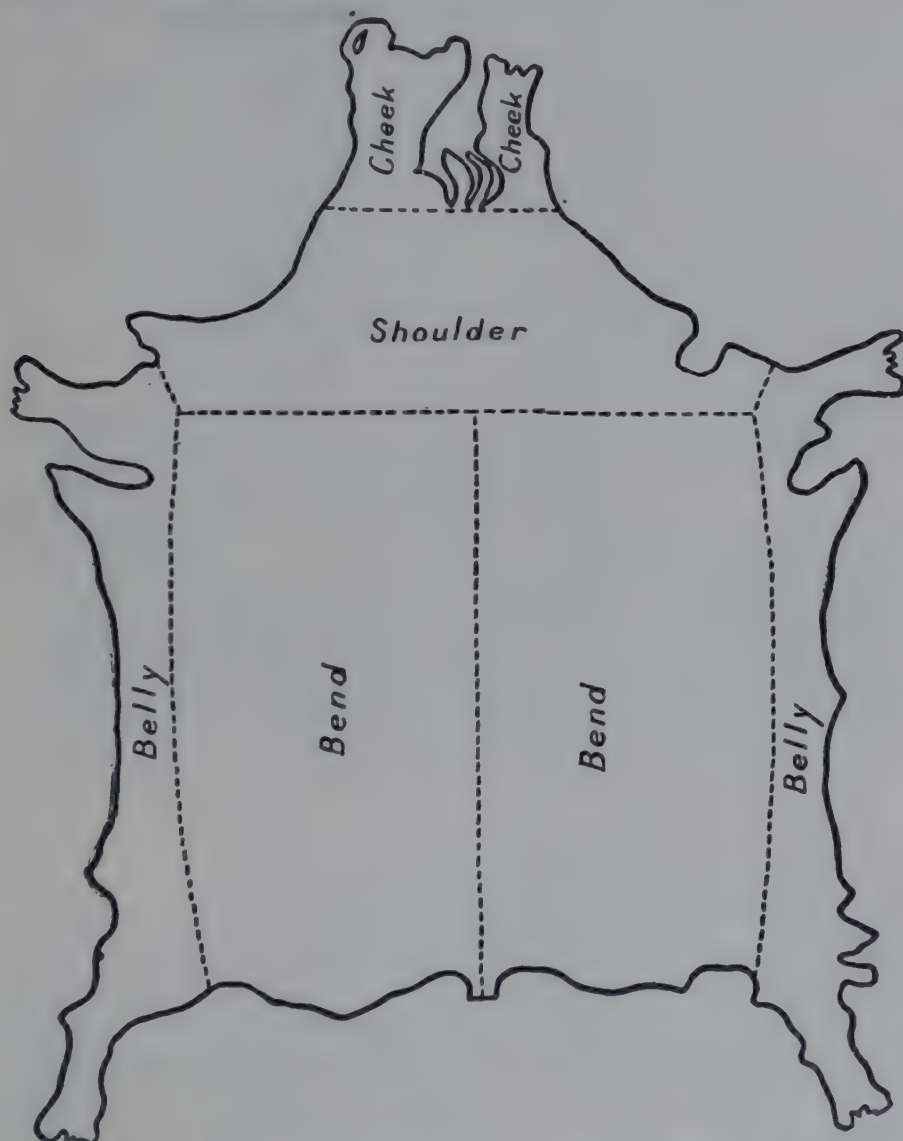


FIG. 230.—Diagram of Rounded Hide.

For even penetration of the tan a gradual increase in strength of each liquor into which the hide is removed is necessary, since diffusion will only take place from a region of higher concentration to that of a lower. The first pits into which the goods are placed are the "handlers"; the hides fastened on poles by one edge are hung vertically in the liquors and frequently moved, whereby the grain is fixed and an even colour is produced. The percentage of tannin in the handler liquors is low and the acidity relatively high (up to one-twentieth normal or even  $\frac{N}{10}$ ).

These conditions are usually attained by working the liquors "down the yard," *i.e.*, the pit from which a pack of goods has just been removed to go into the next stronger one of the series becomes the one below, and its place is taken by the one above it; thus the goods move in one direction and the liquors in the opposite. This system is also advantageous in that the astringent tannins have

already been removed by the goods, leaving only the milder tannins which are more suited to the green goods. The time occupied in the progress of the goods through the suspender varies from ten days to a fortnight; they then pass on to the "handlers." These are worked in systems of six, eight, or ten pits, and the goods are moved forward after being in each pit from six to eight days. The goods are in the handlers for a month to six weeks, and pass from a strength of liquor of about 20° Barkometer\* to that of about 40° Bkr.

By the time the goods leave the handlers they will usually have become completely penetrated by the tan liquor, and the remainder of the tanning process has for its object the deposition of solidifying and weight-giving matter in the interfibrillar spaces. The final step in the tanning process is the laying away of the goods in the "layers" with ground tanning material dusted between each hide and the whole covered with strong tan liquor. By this means the hide is enabled to take up the more difficultly soluble tannins, and a solid and dense leather is the result. The goods are drawn several times and laid down again with fresh quantities of tanning material and stronger liquors, which may reach a strength of 120°-150° Bkr. where extract is used. The time in layers may extend from three to six months.

Of the materials used in the tannage of sole leather, oak bark is one of the oldest and gives a result which is said to be superior to that obtained by any other material, but its low percentage of tannin and the lightness in weight of the finished leather tanned in this way have caused its replacement in many cases by extract. Valonia is used to a great extent, as it gives heavy and solid leather and deposits much bloom. Gambier is used to some extent, the mildness of its tannin making it especially suitable for the strengthening of the suspender liquors. Oak wood, chestnut wood, and hemlock bark extracts are very largely used, principally for strengthening the layer liquors.

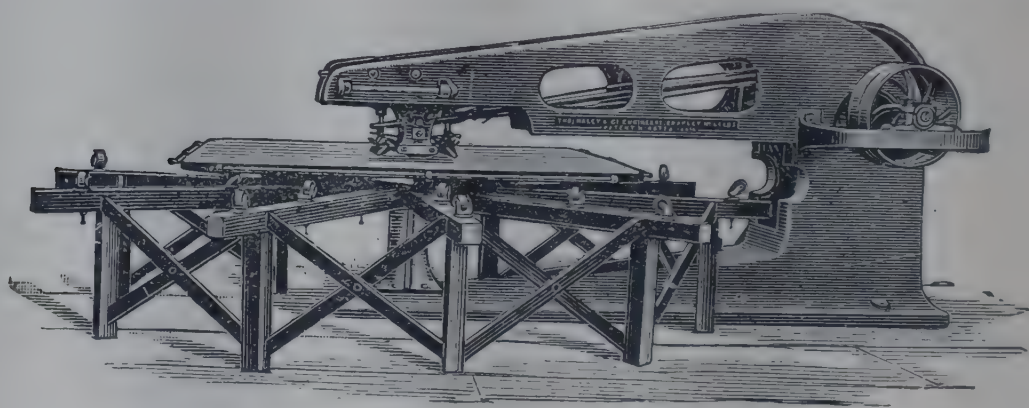


FIG. 231.—Jackson Scouring Machine.

The process of **tanning dressing leather** is similar to that for sole leather, with the difference that as resulting leather is required to be soft and flexible the process is modified accordingly. A lighter class of hides are used, such as kips, or the goods are reduced in substance by shaving. The main point of difference in the method is the introduction of the "bating" process. This consists in submitting the goods to the action of a fermented infusion of hen or pigeon dung. The proportions used are variable, ranging from 12-60 l. per 1,000 kilos. raw hide in 2,000 l. of water. By this means a great portion of the lime is removed and a considerable solution of hide substance occurs. The mechanism of the action of the "bate" is probably analogous to that of the puer (see p. 580). The hides after becoming soft and fallen are usually "scudded" over the beam, in which process much dirt and grease are worked out, and then frequently given a further treatment in an acid bath to remove the last traces of lime before entering the tan liquors.

The tanning is usually commenced, in this country, in paddles, but suspenders are used where a very smooth grain is desired. As bloom is not required in this tannage the use of bloom-giving tanning materials is avoided.

Sole leather after leaving the layers is washed through a clean liquor or warm water, and "scoured" with stone and brush by hand or by machine (Fig. 231) till

\* The Barkometer is a form of hydrometer, and is of great service in controlling the strength of liquors of which the composition is the same. As it shows all solid matter in solution, however, the strength of a liquor in tannin, as shown by it, can only be relatively correct.



all bloom is removed from the grain surface, half dried ("sammed") and laid in pile to temper. A treatment in a strong liquor made from sulphited quebracho extract is frequently given, which results in a better colour in the finished leather though producing considerable loss of weight by the action of the sulphite on the

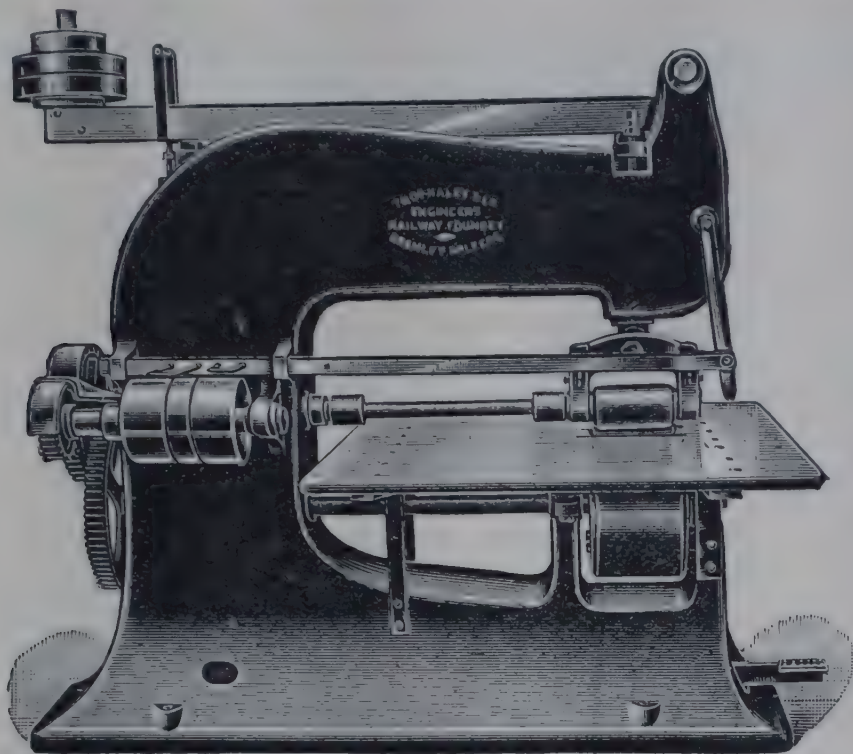


FIG. 232.—Rolling Machine.

tannin held in the leather. It is then "struck out" either with the "pin" or by machine which smooths and flattens the grain. The goods are then rolled by machine, once with a light roller when the grain is somewhat moist, and finally, when nearly dry, with the heavy roller (Fig. 232). They are then dried by the aid of moderate heat, and after polishing with a brush are ready for sale.

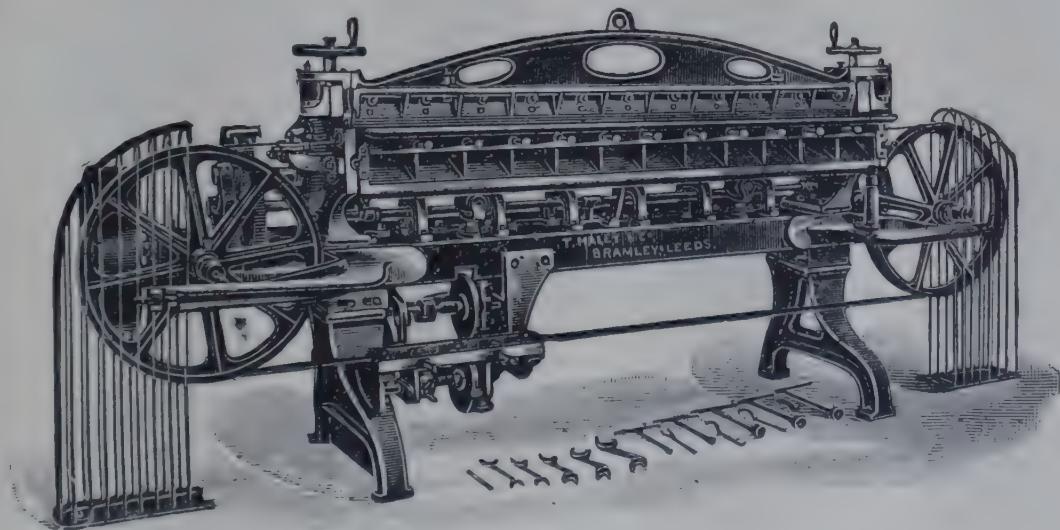


FIG. 233.—Band-Knife Splitting Machine.

A light coating of oil is frequently applied to the grain side before drying in order to cause the evaporation to take place through the flesh side, as otherwise the uncombined tannin would be deposited on the grain and, oxidising, cause the latter to be brittle and of a bad colour.

The **finishing of dressing leather** (for strap butts, harness, belting leather, etc.) differs essentially from that of sole leather in the inclusion of the "**stuffing**"



**process**; this consists in impregnating the leather with a mixture of solid and liquid fats and greases, rendering it supple and impervious to water. The leather is scoured with stone, brush, and sleeker to remove bloom, and reduced in thickness. This is done by shaving by hand or machine, or by splitting the goods.

Shaving by hand requires great skill and is done over a nearly vertical beam with a two-handled knife (Fig. 229) with an edge turned at right angles to the surface of the blade. Of splitting machines for this purpose the band-knife machine (Fig. 233) is the most important; with this machine the leather is held and moved forward by rollers against the edge of an endless ribbon-knife, passing round a wheel at either end of the machine.

The leather must be in a moist state before stuffing, and the exact degree of dampness is a matter of some importance. It should generally be such that water exudes from the pores when the leather is pinched.

The two methods of stuffing most commonly in use are hand stuffing and drum stuffing. In hand stuffing the leather is coated on the flesh side or on both sides with a mixture of fats known as "dubbing," consisting usually of cod oil and tallow. The mixture is melted together and stirred as it cools in order to obtain a homogeneous pasty mass, and the proportions of hard and soft constituents are modified according to the season and the temperature at which the leather is to be dried. Much of the solid crystalline fats remain on the surface of the leather after the remainder has penetrated to the interior, and are scraped off with the sleeker and used again. The temperature at which the stuffed leather is dried is adjusted so that the dubbing is kept in a soft condition, but not so high as to render it liquid.

In "drum stuffing" the goods are treated in a revolving drum (Fig. 234) with the stuffing mixture. The drum, previous to putting in the goods, is heated by blowing in hot air or steam, or frequently a steam coil is fixed in the drum itself. The temperature of the interior of the drum may be safely raised to 60° C. if cold, damp leather is introduced. After the goods have been drummed sufficiently long to have reached the temperature of the interior the stuffing grease is introduced either through the door or run in through a hollow axle. A very large quantity of grease can be taken up by leather without detriment to its light colour which reappears on bending sharply in "boarding." Advantage is frequently taken of the facility with which adulterants can be introduced into the leather in drum stuffing; glucose and barium sulphate are the most common of these, and produce a fictitious weight together with an improved colour to that obtained by an equivalent quantity of grease.

A method of dry stuffing practised in Germany is termed "Einbrennen." Melted tallow is poured over the leather, which must previously have been completely dried, and allowed to sink in by holding over a fire. Another method is to dip the leather completely into molten tallow.

Stuffed leathers are particularly liable to a defect known as "spueing," which is of two kinds. The first, which is by far the least objectionable, is due to the crystallisation of the hard fats on the surface of the leather, and causes no injury to the leather. The other kind is due to a chemical change taking place in the stuffing materials, and makes its appearance as resinous spots or pimples on the surface of the leather. It is usually attributed to adulterated oils, but occasionally appears when the purest cod oil has been used. As it is caused by oxidation of the oil, it is liable to appear when conditions are such as to favour this action, such as moist heat with little ventilation and the catalytic action of iron salts used in the production of black goods.

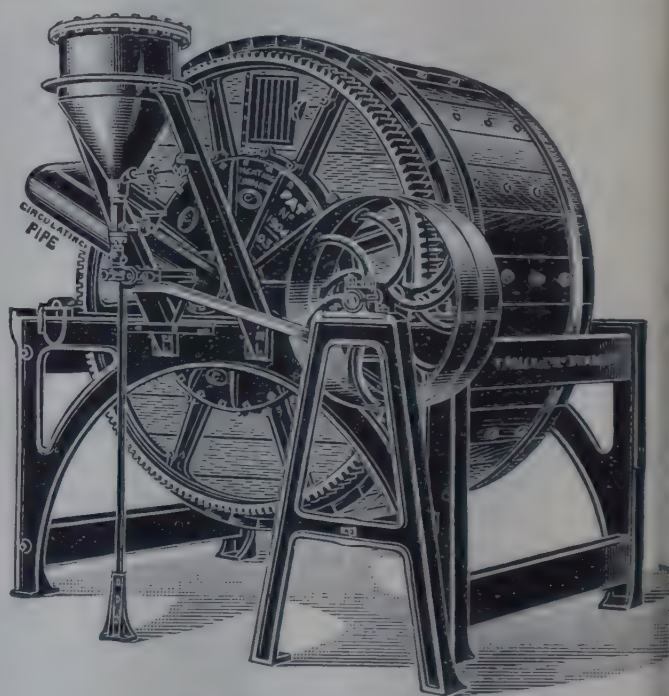


FIG. 234.—Stuffing-Drum.



Fats and oils are also introduced into the leather by "fat liquoring." In the preparation of a fat liquor the oil is reduced to an extremely fine state of division by the use of suitable emulsifying agents. By drumming the goods with such a mixture they may be made to take up a large quantity of oil without acquiring a greasy feel.

Recent views on finishing are as follows:—

There appears to be a tendency towards the adoption of water pigment finishes based on casein in place of cellulose nitrate finishes. Except in the cases of morocco leather and upholstery leather, 80 per cent. of finishing is carried out by means of water pigment finishes.

Modified water finishes have come into prominence recently. Dispersions of synthetic resins of the acrylic family are particularly useful in conjunction with water finishes for obtaining better adhesion, flexibility, and slightly improved water-fastness.

It is intended to replace casein by these synthetic resins entirely when suitable mixtures have been devised. The ultimate aim is to obtain a synthetic resin finish which renders the leather completely waterproof after the dispersion has dried out. There has been some difficulty in pigmenting some dispersions of these waterproof resins.

### Light Leather

The raw material for the manufacture of light leather may be taken as consisting of the skins of sheep, goats, and calves. The method of treatment up to the end of the liming process is practically the same as that for heavy leather except that the liming of sheep and goat skins is usually of a somewhat longer duration, as a soft and supple character in the finished article is required. Sheep skins are usually received at the tan-yard from the fellmonger after the wool has been removed, so the only object of the liming process is to plump the skin and render it in a suitable condition to take up the tannin from the liquors. The main difference between the tanning processes of light and heavy leather is in the condition in which the goods enter the tan liquors. By the treatment subsequent to liming the skins are almost entirely deprived of lime and brought into a soft and flaccid condition, which is essential in order that the finished product may possess the qualities required in this class of leather. A great proportion of sheep skins are split when fully limed and the grain split tanned into "sumac skivers," while the flesh split is oil tanned. A sheep skin tanned by a vegetable process without splitting is termed a "roan" or "basil." The goods, after fleshing or splitting, are washed in paddles in order to remove some of the lime. A little acid is frequently added to the water in the washing paddle in order further to promote this action. The goods are then "**puered**," which operation consists in paddling in a weak warm infusion of fermented dog-dung. By this means a further quantity of lime is removed, and considerable solution of skin substance and emulsification of fats takes place.

The mechanism of the puering process has been investigated by J. T. Wood, who has shown that the effect on the skins is due to the joint action of amines and their compounds, and enzymes produced by the metabolism of bacteria which exist in the puer liquor in great quantity. Wood has found that a puer liquor which has previously been boiled and so freed from living organisms and enzymes has still considerable action on limed skin owing to the removal of lime by the action of amines and their compounds. The liquor treated in this way, however, had no dissolving action in the interfibrillar substance, and did not produce the characteristic properties of puered skin. By precipitating enzymes from a puer solution with alcohol and redissolving in water it was found that the solution had a pronounced puering effect. A mixture of the two classes of active bodies was found to puer a skin in a satisfactory manner.

The puer is usually obtained from the kennels and, coming from this source, contains less lime than usual; it is allowed to ferment for some weeks before use, by which its activity in the direction required is much increased.



A perfectly satisfactory substitute for dog-dung for puering all classes of goods has yet to be discovered. The earliest scientific attempt at providing a substitute was made by Wood, Popp, and Becker with "**Eroding**," by the use of which perfectly satisfactory results may be obtained with some classes of goods. Eroding consists of a solid nutrient medium together with a pure culture of bacteria which have been found to be especially active in the puering process. The nutrient medium is dissolved and suspended in water which is raised to a temperature of 104° F., and the pure culture of *Bacillus erodiens* added. The bacteria are allowed to grow in the medium for about three days, and the temperature is raised to 104° F. every night and morning during that period by admitting steam to the culture. The liquid is then diluted and used in the same manner as a natural puer liquor.

Of the later puer and bate substitutes brought on the market, "**Oropon**," manufactured by Röhm & Haas, Darmstadt, is being used to a great extent. This consists of a mixture of ammonium chloride and pancreatic enzymes held in fine sawdust as inert material.

The operation of puering is one requiring great experience and care to obtain the best results. If the temperature is allowed to become too high, or the skins left in puer liquor too long, the goods may be badly damaged or even completely destroyed by excessive bacterial action. Frequent change of position is necessary in order that the action may be regular, so the goods are usually kept in motion during the whole operation by means of the paddle. The skins are removed from the paddle when sufficiently "fallen," a point to determine which requires a practised touch and great experience. The goods are then "scudded" on the flesh side with a blunt knife by which treatment much grease and dirt are worked out; the operation is sometimes carried out by machine.

The skins are then "**drenched**," which consists of submitting them to the action of a fermenting infusion of bran, and removes a still further quantity of lime and causes slight plumping.

J. T. Wood and Willcox \* have also studied the action of the bran drench upon skins, and have found that the acids produced in the bran fermentation are the active agents in removing lime and plumping the goods. Wood gives the following typical analysis of the acids found in a working drench:—

Formic acid	-	-	-	-	-	0.0306 g. per litre.
Acetic acid	-	-	-	-	-	0.2402 " "
Butyric acid	-	-	-	-	-	0.0134 " "
Lactic acid	-	-	-	-	-	0.7907 " "

The most important living organisms found in the drench were two species of bacteria, named by their discoverer *Bacterium furfuris*  $\alpha$  and  $\beta$ . The two were very similar in character, but produced a slightly better fermentation together than when used separately. The same liability to damage of the skins is present in the drenches as in the puer liquors, particularly through a butyric fermentation which may take place in hot weather, resulting in rapid swelling and solution of the skins.

The quantity of bran used in the drenching process is variable, but an average of about 5–10 per cent. on the weight of the skins is usually taken and infused in water in the proportion of about 4 parts of bran to 1,000 of water. The mashing is carried out at a temperature of about 90° F. and fermentation started by adding a few pailfuls of a working drench. The goods are then added and as the fermentation proceeds are brought to the surface by the gas which is evolved in great quantity during the fermentation.

Thin skins may be drenched sufficiently after the first "rising," but heavier goods are put down several times before sufficiently acted upon. Experience is necessary in judging the point at which a skin is sufficiently drenched, the feel of the goods affording the best criterion. The skins become white and soft and retain the impression made when pressed with the finger.

The use of the bran drench has been to some extent replaced by that of acids, of which lactic acid is the most commonly used. The goods are paddled in a solution of about 2 lbs. of the acid in 100 gals. of water at a temperature of

\* *Journ. Soc. Chem. Ind.*, 1890, 27; 1893, 422; 1897, 510. "Brit. Ass. Rep.," 1893, 723.



30°–35° C. The process is quicker and safer than that of using bran, but the effect produced on the goods is not exactly the same.

The "C.T. Bate" manufactured by the Martin Dennis Chrome Company is also used for removing lime, and is suitable for use as a substitute for drenching. It consists mainly of the sulphonic acids of naphthalene and probably other hydrocarbons, and its antiseptic character may also render it useful in arresting putrefaction.

Gallic acid is capable of bating and its use as such has been patented. It is probably the active agent in the fermented infusion of babool pods, which is much used in India for deliming.

### Tannage of Light Leather

The materials used in the vegetable tanning of light leather are very various. Previous to entering the tanning pits the goods are usually treated in the paddle with a very weak solution of the tanning material, where they remain until coloured through. The movement obtained by paddling is essential in causing even absorption of the tannin and producing a fine grain. In some cases the entire operation of tanning is carried out in the paddle, notably in the tanning of sumac skivers.

After colouring through, the goods are passed through a series of pits in a manner similar to that of heavy leather tanning. The strength of the liquors, however, is much less as is also the acidity of the earlier liquors, as no solution of lime is necessary, it having been almost completely removed in the earlier treatment as described above. Materials which yield "bloom" and a solid character to the leather are avoided, as the main results aimed at in the manufacture of light leather are suppleness and the best possible appearance of the grain. A great proportion of sheep skins are tanned into sumac skivers after splitting when fully limed.

A common process to which the goods are submitted previous to entering the sumac liquors is that of "pickling." After leaving the drenches the grains are paddled in solution of common salt and acid. The usual acid employed is sulphuric acid, on account of its cheapness, but the use of organic acids such as acetic and formic acids has lately been recommended, and has some advantages. A drawback to the use of sulphuric acid is the tendency which traces of it left in the leather have to cause rottenness after the lapse of time.\*

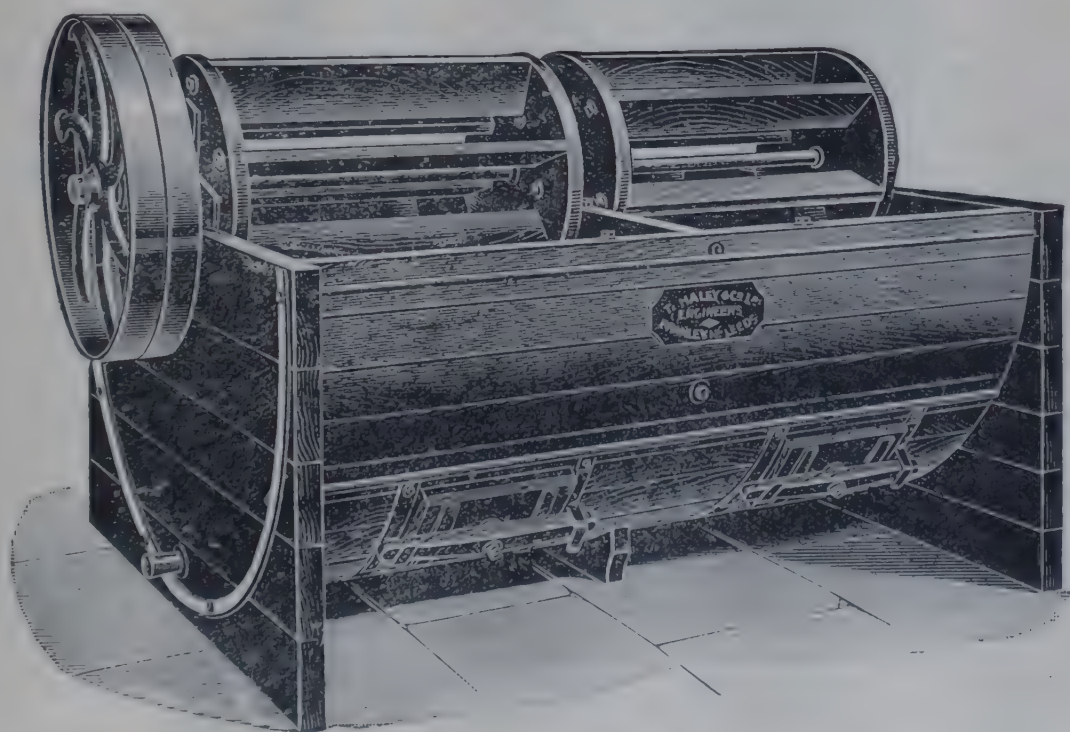


FIG. 235.—Paddle.

\* *Soc. of Arts Journ.*, 1901, 14.



After the uniform penetration of the acid and salt the goods are placed for a short time in a saturated solution of salt. The pickling process permits the skin to be kept for any reasonable length of time in an unchanged condition, and is resorted to when goods are to be exported in the untanned condition. The liquors in which pickled goods are tanned must contain a certain quantity of salt as fresh water produces a strong swelling action on the goods.

The skins are then placed in the paddle (Fig. 235) with water and ground sumac, and kept in circulation until the tanning is complete. The light character of the skins and the movement of the paddle combine to render the tanning operation very short.

A method of tanning with sumac sometimes used consists in sewing each two skins together in the form of a bag, with the grain on the outside. The interior is filled, through a small hole, with strong sumac infusion and some powdered sumac, and after closing the aperture the skins are floated on a warm sumac liquor. After leaving in the liquor for a short time the skins are placed in a pile, and the sumac infusion is forced through the pores of the skins by their own weight. The process is repeated once or twice, which results in the skins being fully tanned in a very short time. A similar method is employed in the manufacture of morocco leather from goat skins.

As stated above, the method of tannage of basils and calf skins with bark and vegetable extracts resembles that of sole leather, except that weaker liquors are used throughout the series of pits, and that the goods are not usually laid away with the solid material to complete the process.

Improvements in tanning technique in recent years tend to pay attention to the control of acids and salts in tan liquors, resulting in quicker tanning, better penetration, and evenness.

### Dyeing

The skins of sheep naturally contain a large quantity of animal grease which must be removed before a level dyeing can be obtained. This is done either by hydraulic pressing before tanning or by the use of a solvent after the tanning process. The dyeing of vegetable-tanned leather is performed either in the tray or in the drum or paddle. In the former method the skins are usually

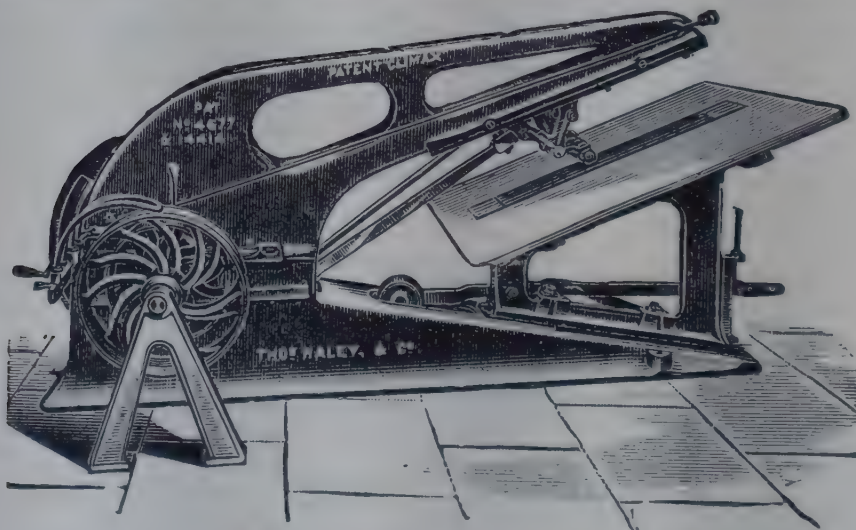


FIG. 236.—Glazing Machine.

dyed in pairs, each pair being pressed firmly together, flesh side in, which results in the flesh side remaining undyed. This results in a saving of dye and a white flesh side which is desirable in some classes of goods. Dark coloured or stained leather is improved before dyeing by treatment with a 1–2 per cent. sulphuric acid solution or preferably with an organic acid.

The use of aniline colours has for the most part replaced that of the natural colouring materials, except in the production of blacks for which logwood is still used to some extent.

Either acid or basic colours are used; in the latter case a mordant such as tartar emetic is used. Titanium potassium oxalate has lately come into use to a great extent, the yellow colour which it produces in combination with tannin rendering it of great use when similar shades of colour are to be applied to the leather. When acid dyes are used, it is customary to add a small quantity of acid to the dye bath for the purpose of liberating the colour acid.

Another method of dyeing which is used to some extent for light leather and almost universally for the heavier leathers is that of staining. In this method the colour is applied to the slightly damp surface of the leather by means of a brush, several coats being given if necessary with partial drying between each application.



After dyeing the grain surface of the leather is rendered glossy and smooth by the application of a "finish" of a mucilaginous nature, or by the use of a seasoning preparation followed by glazing by machine (Fig. 236).

Recent views on the dyeing of leather are as follows:—

The azo-dyes are favourites. Attempts are being made to evolve dyes which have surface-dyeing properties. These dyes can be mixed in any proportion to give a good level of dyeing and the same rate of penetration. Surface dyeing is, of course, preferred for most leathers because it gives the most colour value on the surface. In the case of suède, however, complete penetration is usually required and for this purpose azo-dyes are used in the presence of ammonia to give a high pH. When extreme surface dyeing is required the parts of the skin to be dyed are treated with a cationic wetting agent. This reacts with the anionic azo-dye precipitating the latter in the form of a lake on the surface. These cationic wetting agents can also be used to cause penetration of the basic dyes.

Most of the usual troubles in leather dyeing can be traced to faulty dressing or tanning of the skins. Uneven distribution of the chrome will cause uneven absorption of the dye. It is recommended that for leather dyeing the strength of the dye should be the maximum possible. The use of salt or other electrolyte for standardising dyes to a given strength is not to be recommended for leather dyeing for the following reason. Supposing 20 per cent. of dye was used in a solution for dyeing suède. When we use instead one of the standardised dyes (containing, say, 50 per cent. electrolyte), 40 per cent. would have to be used to obtain the same depth of dyeing. This means that the dye liquor would contain 20 per cent. of electrolyte which not only tends to throw the dye out of solution but causes the leather to absorb large quantities of salt which will very likely return to the surface later.

When pastel shades are required it is usual to block some of the affinity of the skin by a so-called colourless dye, *e.g.*, naphthalene sulphonic acid. Subsequent treatment with the dye proper gives a weak colour with greater penetration.

### Chemical Control of the Tanyard

The quantitative analysis of the vegetable tanning materials presents many difficulties, and it is only by strict adherence to standardised methods of analysis that different workers can obtain concordant results. The International Association of Leather Trades' Chemists have formulated rules for the sampling and analysis of tanning materials, and reference should be made to these for details of the process.

**The Löwenthal Method** of tannin analysis requires the following solutions:—

1. Potassium permanganate, 0.5 g. per litre.
2. Sodium sulphindigotate, 5 g., and strong sulphuric acid, 50 g. per litre.
3. Pure tannin, 3 g. per litre, for determining the tannin value of the permanganate.

25 c.c. of the indigo solution is placed in a beaker and diluted with  $\frac{3}{4}$  l. of tap water. The permanganate solution is then run in from a burette until the colour becomes a pure yellow. 5 c.c. of the tan liquor is then taken in addition to the indigo and the titration repeated.

The difference between the two titrations represents the total oxidisable matter present in the liquor. The liquor is then detannised in the following way: 25 c.c. of 2 per cent. gelatine solution, and 25 c.c. of saturated salt solution containing 50 c.c. concentrated sulphuric acid per litre are added to 50 c.c. of the liquor and shaken for five minutes and filtered with the addition of kaolin if necessary. The filtrate is titrated in the same manner with the permanganate, twice the volume being taken to allow for the dilution. Detannisation is more conveniently done by shaking with hide powder, as in the official method, or with chrome shavings if available. The amount of permanganate equivalent to the tannin in the solution is thus equal to the difference of the titrations before and after detannisation. By determining the permanganate value of the standard solution of pure tannin the strength in tannin of the liquor may be easily calculated.

**Acidity** of tan liquors is determined by Procter's method by adding saturated lime water from a burette to 10 c.c. of the perfectly clear liquor in a beaker till the first trace of permanent turbidity appears.

### The Analysis of Leather

The complete analysis of a sample of vegetable tanned leather consists in the determination of: (1) Water; (2) fatty matter; (3) water soluble matter, including—(a) uncombined tannins, (b) non-tannins; (4) insoluble matter, including—(a) hide substance, (b) tannin.



**Water** is determined by drying finely divided leather at 100° C.

**Fats** are determined by extracting with petrol ether in a Soxhlet apparatus.

**Water soluble matter** is estimated by digesting the extracted residue from the fat determination for some hours with 200 c.c. of distilled water at 15°-20° C., and then extracting in a similar method to that employed for tanning materials. The temperature of the water used for extraction is kept low to avoid decomposition of the leather. The proportions of tannin and non-tannins in the extract are differentiated as in the analysis of tannin materials by determination of total solids in the solution before and after detannisation.

Glucose and mineral adulterants, such as magnesium sulphate, if present, will be found in the non-tannin portion of the extract. Glucose is determined with Fehling's solution after removal of the tannin, etc., by precipitation with basic lead acetate.

**Hide substance** is estimated by determining the nitrogen (Kjeldahl method) in the original sample.

Since hide substance contains approximately 17.8 per cent. nitrogen, the percentage of nitrogen is multiplied by the factor 5.62.

The estimation of **free mineral acid** is very important, and is best carried out by Procter and Searle's method. 2 or 3 g. of the finely divided sample are moistened in a platinum crucible with 25 c.c. of  $\frac{N}{10}$  sodium carbonate solution, evaporated to dryness, thoroughly carbonised, extracted

with boiling water, filtered, and the residue ignited in the crucible. 25 c.c. of decinormal hydrochloric acid is then added to the ash, and the whole is added to the filtrate previously obtained. If the solution is then alkaline, free mineral acid may be assumed to be absent, but if acid the amount may be measured by titration with decinormal alkali using methyl orange as indicator.

The quantitative and qualitative examination of the leather **ash** will often afford valuable information with regard to the tannage, etc.

### Mineral Tannages

Of the mineral tanning processes, the most important is that involving the use of the salts of **chromium**. The process has already become a very serious rival to the vegetable tannages, and even, in some cases, has replaced them to a great extent.

There are two general methods of tanning with chromium compounds known respectively as the "one-bath" and the "two-bath" processes. In both methods the actual tanning agent is the same, the fibres being isolated and rendered imputrescible by the deposition on them of a basic chrome salt. In the one-bath process this is accomplished by immersing the skin in a basic solution of chromium sulphate or chloride, while the two-bath process consists in saturating the skin in a solution of chromic acid, and then submitting it to the action of a reducing bath whereby the actual tanning agent is formed in the interior of the skin. Professor Knapp in 1858 was the first to devise a practicable chrome tanning process which consisted in treating skins with a basic chromium chloride solution made by adding sodium carbonate to a solution of normal chromium chloride. The process was revived and patented later by Martin Dennis,\* who put on the market a basic chrome tanning liquor prepared by dissolving chromium hydrate in hydrochloric acid, and rendering sufficiently basic with sodium carbonate.

The earliest two-bath process was proposed by Augustus Schultz in 1884. The method as patented by him consisted in paddling or drumming skins in a solution of 5 per cent. bichromate of potash and  $2\frac{1}{2}$  per cent. hydrochloric acid or an equivalent amount of sulphuric acid, till evenly coloured through with the chromic acid. The second bath consisted of a solution of sulphurous acid or an acidified solution of sodium thiosulphate.

The **one-bath process** is, of the two, the more analogous to the vegetable tanning process. Eitner† has shown that the basicity to which the chromium salt is brought is of extreme importance. A solution of a normal chromium salt penetrates the skin with great rapidity, but is very easily washed out, and a thin and lightly tanned leather results. As the salt is rendered more basic the rapidity of

\* U.S.A. Patent, 495,028, 1893; 511,411, 1893; 7,732, 1893.

† Gerber, 1901, 3.



its penetration into the skin is less, but its absorption is more thorough, and the chrome is fixed more strongly. If the basicity, however, is rendered excessive, part of the chromium is precipitated as hydrate, and an insufficiently basic salt is left, resulting in very slow penetration of the tanning agent and overtanning at the surface of the skin, whereby the grain is rendered tender and even brittle.

Eitner considers as the most suitable the salt  $\text{CrOH}, \text{SO}_4$ , which is produced by the addition of 106 parts by weight (1 molecule) of dry sodium carbonate to 998 parts (1 molecule) of chrome alum.

Procter\* has published a method of preparation of a one-bath solution by the direct reduction of bichromate with sugar in the presence of such a limited amount of hydrochloric or sulphuric acid as to result in a chromium salt of the required basicity. Suitable proportions are 5 molecules of  $\text{HCl}$  to 1 molecule of potassium dichromate, which results in the formation of a salt of approximately the formula of  $\text{Cr}_2\text{Cl}_3(\text{OH})_3$ .

A stock one-bath chrome liquor may be made by dissolving 10 parts of chrome alum in 80 parts of warm water and adding, with constant stirring, a solution of  $2\frac{1}{2}$ - $3\frac{1}{2}$  parts of washing soda dissolved in 10 parts of water.†

Stock liquors which are bought ready made up and only requiring dilution with water are used to a great extent.

The product of the **two-bath process** differs from that of the one-bath in containing free sulphur, which is deposited in the leather from the decomposition of the thiosulphate used in the reduction.

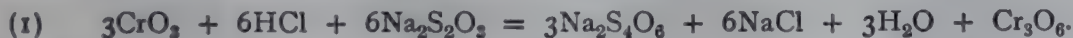
In the first bath the following reaction takes place:—



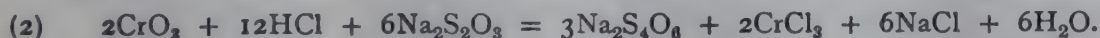
the free chromic acid being absorbed by the skin. Heal and Procter‡ have shown that pelt absorbs no free chromic acid from a solution of potassium dichromate unless free chromic acid has previously been formed by the addition of acid.

The reactions taking place in the second bath have been studied very carefully by Eitner,§ who has shown that the following reactions take place when acid is added gradually to the thiosulphate solution.

On the addition of a small quantity of acid the skins become brownish from the formation of chromium dioxide or basic chromic chromate,  $\text{Cr}_2\text{CrO}_4(\text{OH})_4$ .



On adding more acid the colour of the skins becomes brighter from the formation of chromium chloride.



Further addition of acid results in the deposition of sulphur, partly in the skins and partly precipitated in the bath.



After all the acid has been used up, further reactions take place between the chromium salts and the excess of thiosulphate, resulting in the formation of basic chromium salts and of more free sulphur.



As the acid is, in practice, added in small quantities at a time the reactions will take place, in the main, according to these equations, but will always to some extent proceed simultaneously.

The proportions of dichromate and acid in the first bath, as used in practice, are very variable, the more important constituent being the acid, as it is only the free chromic acid which is thereby liberated which is absorbed by the skins. In Eitner's first bath sufficient acid is added to liberate the whole of the chromic acid, but a less quantity than this is frequently used. Absorption of the chromic acid by the skins is very rapid, and by drumming in the solution the skins are soon caused to take up the maximum amount. After leaving the first bath the goods

\* *Leather Trades' Review*, 12th January 1897.

† *Ibid.*

‡ *Journ. Soc. Chem. Ind.*, 1895, 251.

§ *Gerber*, 1900, 297.



are piled on a "horse" and allowed to remain so for some hours or overnight, whereby better fixation of the chrome is obtained. When in this state the goods are carefully protected from the action of light, which results in the reduction of the chrome at the expense of the skin and thereby causes irregular tanning.

Before entering the second bath the skins are frequently drawn through a strong "hypo" bath in order to fix the chrome on the surface of the skin which prevents "bleeding," *i.e.*, diffusion of the chromic acid solution into the hypo bath. The most usual reducing agent is a solution of sodium thiosulphate ("hypo") rendered acid with hydrochloric acid, and in this bath also great variations in the proportions used are met with in practice. It is usual to add the acid in small quantities at a time as the reduction proceeds, as the reduction is rendered more even and there is less loss by escape of sulphur dioxide into the air. Eitner suggests 12 parts of hypo dissolved in 400 parts of water, and 6 parts of 40 per cent. hydrochloric acid per 100 parts of wet pelt, less acid, however, being required if equal parts of acid and dichromate have been used in the first bath.

The operation of neutralising follows that of tanning, and is carried out in the same manner for leather tanned by either of the processes. When a two-bath process has been used the skins contain a considerable quantity of free acid which must be removed; and with one-bath leather the neutralising process results in further fixation of the chrome in the leather fibre. The skins are drummed in a dilute solution of a weak alkali of which several are in use, such as sodium bicarbonate or dilute ammonia. Borax is used to a great extent, its weakly alkaline nature rendering it the safest neutralising agent, and lessening the danger of over-neutralisation. The neutralising process is considered to be complete when a piece of blue litmus paper is not turned red on application to the freshly cut surface of the skin. Over-neutralisation to the extent of rendering the interior of the skin distinctly alkaline is carefully avoided, as the presence of free alkali in the skin is as objectionable in its effects as that of free acid. Eitner has recommended the use of silicate of soda as a neutralising material, and sodium hyposulphite and whitening have also been used. After neutralisation the goods are thoroughly washed in the drum in a stream of running water.

A peculiarity of the chrome process is that the goods are usually dyed and fat-liquored immediately after tanning, as if they are once allowed to become thoroughly dry it is impossible for them to be "wetted down" again sufficiently for even dyeing.

Fat liquoring, which is done either before or after the dyeing process, consists in drumming the skins in an emulsion of soap and oil which is absorbed very readily, and gives a plump and soft feel to the leather which would otherwise, from the nature of the tannage, be harsh and empty.

Many different formulæ for the preparation of fat liquors are in use, and various oils, such as castor, olive, cod, and neat's foot, are suitable. Sulphonated or turkey-red oils have lately been used to a great extent, and being soluble in water need no addition of soap as an emulsifying agent.

By drumming with a solution of glycerol or sugar chrome leather may be dried sufficiently to allow of the operations of shaving or staking before dyeing, the hygroscopic nature of these bodies rendering it possible to wet down the leather subsequently sufficiently for dyeing.

Recent work suggests that there will soon be available emulsifying agents which can be destroyed by the drying or warming up of the skin so that once they have served their purpose by taking the oil into the leather they no longer exist to facilitate its removal. This type of emulsifying agent is not yet on the market.

Chrome leather may be dyed direct with many of the acid aniline colours, but where basic colours are to be used the goods are given a tannin mordant by drumming or paddling with sumac infusion or gambier.

After dyeing the goods are thoroughly dried by hanging in heated stoves, and then, if necessary, the natural animal grease is removed by extraction with a solvent in a plant specially devised for that purpose. They are then brought to the necessary degree of dampness for the subsequent treatment by laying away among damp sawdust. Being now stiff and hard they are softened by staking, which is done by a machine which draws a blunt-edged blade along the flesh side



of the skin, which is held against it by rollers (Fig. 237). The appearance of the grain is then improved by the application of a "finish," which usually contains blood or albumen, followed by "glazing" by friction of a glass or agate "stone" under pressure. This operation is frequently repeated several times, and ironing with a hot iron completes the process.

Of the lighter leathers tanned by the chrome process calf skins, which are manufactured into "**box-calf**" or "**willow-calf**" (usually by the one-bath method), form a large proportion. In the manufacture of these goods, the operation of "boarding" (Fig. 229) (whereby the grain of the leather is raised) is included in the finishing process.

The manufacture of **glacé kid** from goat skins has attained gigantic proportions. Sheep skins are also chrome tanned to imitate real glacé kid.

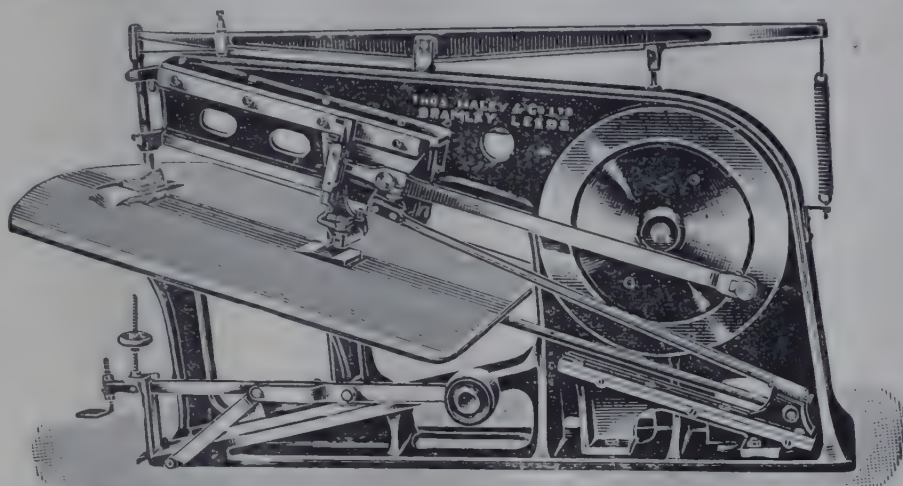


FIG. 237.—Staking Machine.

The chrome process is frequently combined with one of the vegetable tanning processes, the product being known as "**semichrome**." The order in which the two tannages are applied varies, but a one-bath chrome tannage is necessarily used. The method is more particularly applied to the imported native-tanned sheep or goat skins from India (Persians). Before chroming, as much as possible of the vegetable tanning material is removed by drumming the leather in a dilute alkaline solution ("stripping").

### Recent Developments in Chrome Tanning Technique

In the year 1931, Professors H. R. Proctor and E. Stiasny suggested the use of organic acids or salts in chrome tanning liquors to control the properties of the latter. In recent years others have followed up this work and have developed the technique of "masking."

It has been found that when monocarboxylic acids or dicarboxylic acids are added to the chrome liquor the quantity of chrome taken up by the leather is increased when a certain quantity of masking acid has been added. When a further quantity of masking acid is added the chrome uptake is diminished. When different carboxylic acids are used it is found that the maximum uptake of chrome occurs at a fixed ratio of carboxyl to chromium. Apparently a specific Werner complex is formed. It is found that a ratio of 0.5 mol. of dicarboxylic acid to 1.0 mol. of chromium trioxide gives optimum results in chrome tanning. Adipic acid has been found to be the best of many monocarboxylic and dicarboxylic acids tried. It has a carboxyl group at each end of a chain of four methylene groups. If carboxylic acids with a longer aliphatic chain are used the leather tends to become too soft and greasy. This is due to the predominant effect of the aliphatic chain. Phthalic acid has been used as a masking acid, and one school of thought prefers formic acid. The heavy molecule of phthalic acid is said to give greater substance to skins taken from the flanks and bellies. Adipic acid is still preferred as an all-round masking acid.



The great advantage of masked chrome tanning is its speed. A 4 mm. hide is tanned completely in three hours. The chrome uptake from such a bath is extremely high without any special precautions being taken.

### Chemical Control of the Chrome Process

**One-Bath Liquors.**—The chromium in one-bath chrome liquors may be estimated gravimetrically by precipitation as  $\text{Cr}_2\text{O}_3$  with ammonia, but more quickly and conveniently volumetrically. The chromium is converted into sodium chromate by treatment with sodium peroxide and the chromic acid estimated by acidifying, adding excess of potassium iodide and titrating with standard sodium thiosulphate solution. The estimation of the acidity of one-bath liquors, which is of great importance, is most conveniently carried out by the method of Procter and M'Candlish.\* The whole of the acid is estimated in this way by titration of the boiling diluted solution with normal sodium hydrate with the addition of rather a large quantity of phenolphthalein as indicator.

The colorimetric method forms a useful control of spent one-bath chrome liquors.†

**Two-Bath Liquors.**—The chromic acid in two-bath liquors is estimated by titration with thiosulphate solution in the same way as for one-bath liquors.

Free acid is estimated in two-bath liquors by titration with standard caustic alkali with phenolphthalein.

Since normal chromates are neutral to phenolphthalein, and free chromic acid and bichromates are acid to that indicator, the relative amounts of free chromic acid or of bichromate and chromate may be calculated from the results of the above two titrations.

The thiosulphate in a second-bath liquor is estimated by titrating with it the iodine liberated from potassium iodide by a known volume of an acidified solution of standard potassium bichromate.

**Chromium** in chrome leather is estimated by ashing a weighed quantity of the leather in a platinum crucible and converting the chromium to chromate by ignition with a mixture of sodium and potassium carbonate. The chromate is dissolved and estimated volumetrically in the usual manner.

Two-bath chrome leather may be distinguished from one-bath leather by damping and wrapping in paper with a silver coin. After leaving in a warm place for an hour, the coin will become stained brown or black from the formation of silver sulphide from the sulphur in the leather.

### Alum Tannage

The mechanism of the alum-tanning or tawing process is probably the same as that of chrome, the actual tanning agent being regarded as a basic alumina salt.

Small skins which are required to be preserved with the hair or wool on are stretched on a board with the flesh side outwards after cleansing from blood and dirt as far as possible. A strong solution of alum and common salt is applied hot with a sponge, and the application repeated till the skin is struck through. In the manufacture of **glove-kid**, for which lamb skins are used for the most part, and genuine kid skins for the best qualities only, the skins, after liming, puering, and drenching, are treated with a mixture of alum, salt, flour, olive oil, and egg yolks in a thin paste. The mixture is caused to penetrate the skins by being trodden with them or, more usually, by drumming. The goods are then dried rapidly and passed through tepid water and made uniformly moist by treading tightly into chests, in which they remain for twelve hours. They are then trodden on a floor of sharply angular edges formed by bars of wood and subsequently stretched with the "moon-knife" (Fig. 229). The latter consists of a circular knife in the shape of a quoit and is held by the workman by its inner edge and drawn down the flesh side of the skins, which are attached to a horizontal pole by one end, the other being held by the operator. The skins are then dried nearly completely and staked, which consists in drawing them over a blunt knife edge fixed in the top of a post. Staking is also done to a great extent by machine.

\* Procter and M'Candlish, *Journ. Soc. Chem. Ind.*, 1907, 458.

† Wood and Law, *Journ. Soc. Chem. Ind.*, 1910, 398.



The goods are then "aged" from one to three months, which is necessary in fixing the tanning agent and producing the necessary properties of the finished article. They are then dyed after the removal of part of the tawing mixture by treatment with tepid water.

Aniline dyes or natural dyewood colours are used; in the latter case an alkaline mordant is first given, and also usually the colour is made brighter and more permanent by the use of a striker consisting of a salt of zinc, iron, or copper.

The manufacture of **calf kid** is similar to the process just described except that the puering process is omitted, the lime being removed by successive washings and working in the beam.

After drenching, the skins are drummed in the tawing paste, which may consist, according to Procter, of 5 per cent. flour, 2.5 per cent. alum, 1 per cent. salt, the yolks of twenty-five eggs or  $1\frac{1}{2}$  lbs. preserved egg yolk, 2 oz. olive oil, and  $1\frac{1}{4}$ - $1\frac{1}{2}$  gals. of water to 100 lbs. of wet pelt. The skins are penetrated in several hours and allowed to lie in pile overnight and sometimes split, in this condition, in the band-knife machine. They are then dried rapidly and aged for one to three months after damping back and staking by machine. After being thoroughly wetted back, the skins are given an alkaline mordant and blacked with an infusion of logwood or fustic fixed and darkened by a solution of ferrous sulphate. The wetting back causes a loss of part of the tanning material which is replaced by "re-egging" with egg yolk and flour, and sometimes alum and salt. If the goods are blacked on the table the "re-egging" is done previous to dyeing, but if dyed in the tray it is done afterwards, as the dyeing process would result in the removal of a further quantity of the material. After drying again, the goods are softened by staking or perching, and ironed after the application of a composition containing oil and wax, which results in a smooth glossy surface. The process is completed by the application of a final gloss and a small quantity of French chalk.

A large number of processes, combining the use of alum with that of the vegetable tanning materials, are in use.

**Dongola leather**, which is one of the most important products of these combination tannages, is made by handling the skins in a bath containing gambier, alum, and salt.

"**Green leathers**," largely made in the West Riding of Yorkshire, are first given a light gambier tannage and then handled in a hot and strong solution of salt and alum, and finally heavily stuffed with sod oil.

### Oil Tannage

The greater part of the raw material used in oil tannage consists of the flesh split of sheep skins, the finished product being the ordinary "**chamois**" or "**wash leather**." The skins are split after the completion of the liming process, and the loose and fatty middle layer is removed by a sharp knife on the beam ("frizzing"). Part of the lime in the goods is then removed by means of drenching (see p. 581). After draining, as much as possible of the water is removed, either by stocking with sawdust in the fuller stocks or by hydraulic pressing. By this means the fibre is isolated and opened out and the skin rendered porous and easily able to absorb the oil. The goods are then placed again in the fuller stocks (Fig. 228) and cod oil added in small quantities at a time and evenly distributed by the motion of the skins. They are then hung to allow evaporation of the remaining water and penetration of the oil. Care is necessary to avoid any part of the skin drying before absorption of the oil, or hard and transparent patches will result. The processes of oiling, stocking, and hanging are repeated till all the water previously in the skins has been replaced by oil. The goods are then hung in "stoves" heated to a high temperature in which large quantities of irritating vapours are produced by the oxidation of the oils. The oxidation is carried further in the English method by packing the skins in large boxes or tubs in which great heat is spontaneously generated, which would destroy the goods if allowed to proceed. When the maximum temperature, which the skins will safely stand is reached, the goods are removed from the boxes and strewn on the floor to cool. They are then replaced in the receptacles and the process repeated till oxidation is complete and



no further heating occurs. In the French method the oxidation is completely effected in the stove without the use of the packing process.

The goods are then dipped in water and wrung or hydraulically pressed, and the excess of oil thus removed constitutes moellon, dégras, or sod oil, which is an extremely valuable material for use in currying, so much so that skins are frequently oiled and pressed for the sole purpose of obtaining it.

A further quantity of sod oil of an inferior quality is obtained from the pressed leather by paddling with soda or potash solution and recovering the oil by decomposing the soap thus formed by acidification with sulphuric acid.

**Buff leather**, for military accoutrements, is made in a similar manner from hides after removal of the grain by frizing. Bleaching of buff and chamois leather is effected by exposure in a damp condition to sunlight, or by means of oxidising agents.

A similar product, obtained without the use of oils, is the "**Kaspine**" leather of Messrs J. & E. Pullman.\* The goods, prepared as for oil tannage, are treated in a drum with a very dilute solution of formaldehyde rendered alkaline with sodium carbonate. The product is very similar to oil-tanned leather, but needs no bleaching, being white right through.

Various other methods of employing oils and fats in the tanning of leather are in use, of which the "**Crown**" and "**Helvetia**" leathers are the most important products. The method of manufacture of the former, originally devised by Klemm, consisted in treating the prepared skins with a mixture of flour, ox-brains, butter, milk, and soft fat, and drumming in warm drums.

"**Riems**" are made in South Africa by cutting a strip of raw hide, and suspending with a heavy weight on one end after coating with oil. By repeated oiling and twisting the thong is saturated with the oil, and an extremely tough and flexible leather is produced.

**Artificial leather**, a product of recent years, is made by separating into their constituent fibres such substances as waste leather, cotton, paper, felt, etc. (as under **Paper**), then oiling the fibres to render them soft, and cementing them together by kneading with a solution of celluloid, viscose, or caoutchouc in special machines, drying and calendering. The product is used for furniture-covering, stiff wallpaper, and ornamental articles such as cheap ladies' bags, purses, etc.

**Pergament**, or parchment, is not true leather, but consists of calf skins and the flesh splits of sheep skins well rubbed with pumice stone and chalk paste, and dried in a stretched condition. It forms a horny substance, lacking the flexibility of leather; in a damp condition it may putrefy.

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\* English Patent, 2,872, 1892.



## SECTION XX

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The Glue, Gelatine, and Albumen Industry





# THE GLUE, GELATINE, AND ALBUMEN INDUSTRY

Originally written by G. MARTIN, Ph.D., D.Sc.  
Revised by E. I. COOKE, M.A.(Cantab.), B.Sc., A.R.I.C.

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ORDINARY glue is a product of decomposition of nitrogenous matter contained in animal skins and bones. When hides are heated with water they swell up, lose their organic structure and dissolve to a clear solution, which on cooling—even when it contains only 1 per cent. of nitrogenous matter—solidifies to a jelly (“gelatine”) and dries to a transparent mass, known as glue. The dried mass will again dissolve in hot water, giving a solution which has an extraordinary adhesive capacity.

Three main varieties of glue are manufactured: (1) **Hide Glue**; (2) **Bone Glue**; (3) **Fish Glue**.

All these kinds of glue have approximately the same composition (C=49.51 per cent., H=6.5-7.5 per cent., N=17-18.8 per cent., S=0.7 per cent.) and consist of a mixture of protein-like substances, the chief constituent of which is called “**Glutin**.” Glutin has not yet been obtained quite pure, and is an amorphous, tasteless, and odourless substance, which swells up in cold water and passes into a colloidal solution in hot water; it is precipitated from aqueous solution by alcohol and also by tannic acid, the latter uniting with it to form an insoluble compound, probably connected with the insoluble body produced in tanning leather (see **Leather**).

Formaldehyde also renders gelatine and glue insoluble. Alum and ferrous sulphate in the presence of alkali precipitate glutin.

When glutin is boiled with water for any length of time it undergoes further decomposition, yielding products very deficient in adhesive capacity and incapable of forming jellies (see p. 568).

## Manufacture of Hide Glue

Fresh waste from tanneries and slaughter-houses (scraps of hide, earlaps, tails, tendons, feet of oxen and sheep, etc. etc.) is placed in cemented vats filled with thin milk of lime and left for three weeks or less. The lime saponifies fatty matter (forming insoluble calcium soaps and glycerol), and partially dissolves non-gluey matter, such as blood, flesh, coriin, thus making the hide loose and soft. Next, the material is freed from traces of lime (otherwise the product will be inferior) by careful washing and by treating with acid solutions, e.g., dilute sulphurous acid or spent tan liquor. Sometimes instead of liming a treatment with SO<sub>2</sub>, followed by bleaching with bleaching powder, is followed.



The raw product thus obtained is rinsed and then boiled with the proper amount (not too much) of water in open tinned pans, usually provided with a false sieve-like bottom and heated by steam coils or a steam jacket. The glue dissolves in the warm water, but hair and meat remain suspended. The fats and calcium soaps float to the surface and are skimmed off. Long boiling must be carefully avoided as it injures the glue. When solution is complete the liquid is filtered off as clear as possible through the sieve bottoms and run into a vacuum pan and is concentrated at 60° C. (see Fig. 21, p. 81, for a type of the vacuum pan employed). Higher temperatures seriously damage the sticking power of the glue owing to partial decomposition of the glutin. The lower the temperatures used the better the glue. When the concentration reaches 15-20 per cent., the yellow dirty-looking fluid is partially clarified by SO<sub>2</sub> or other clarifying agent.

Complete decolourisation is usually not possible even by the combined action of SO<sub>2</sub> and animal charcoal. Great care must be taken in the use of decolourising agents since they usually seriously damage the glue. Alum, for example, renders much of the glue insoluble, and affects its adhesive properties.

When the proper degree of concentration is attained the glue is poured in a thin layer about  $\frac{1}{8}$  in. thick over large, flat, smooth surfaces usually consisting of surfaces covered with glass plates cooled below by cold water. The glue is thus rapidly cooled and sets to a gelatine. It is then cut up into tablets of convenient size, and rapidly dried at as low a temperature as possible. If the drying is not rapid enough putrefaction may set in, as gelatine is an excellent developing medium for bacteria; if the temperature of drying is too high the gelatine melts. The gelatine tablets are therefore usually laid on netting (its impression showing on the finished article), and dried in a draught of air at 20° C. in special chambers. The tablets thus produced contain about 15 per cent. of water, and a considerable amount of ash. The less the glue has been boiled and the thinner the plates the better the adhesive properties of the product. The value of a glue is tested by actual trial, the chemical analysis having little value as a criterion of its adhesive quality.

Many attempts have been made to use tanned leather or leather wastes for glue making, but with somewhat doubtful success in most cases. Such leather is "untanned" by treating first with alkali, and then with lime. Chrome leather is untanned by dipping in dilute H<sub>2</sub>SO<sub>4</sub>, rinsing with H<sub>2</sub>O, and neutralising with lime. The last traces of lime are removed by HCl, then alkali, and the product is finally washed and boiled for glue.

Trotman (British Patents, Nos. 5,676, 12,393, 1911) decromes chrome tanned leather for the preparation of glue by treating with dilute HCl or H<sub>2</sub>SO<sub>4</sub>, washing, neutralising with alkali, and treating with sodium peroxide which converts the chromium compounds into chromates, which are then removed by washing. The amount of NaOH present is controlled by adding  $\text{CaCl}_2(2\text{NaOH} + \text{CaCl}_2 = 2\text{NaCl} + \text{Ca}(\text{OH})_2)$ . Trotman detans ordinary tanned leather by soaking in alkali, rinsing, treating with sodium peroxide, rinsing, and neutralising with acid.

## Manufacture of Bone Glue

This is prepared by several processes.

(a) **Acid Process.**—The bone is soaked in an 8 per cent. solution of HCl which extracts the mineral matter (calcium phosphate). The stiff cartilage remaining is washed with lime water and dissolved in boiling water as described under Hide Glue.

The acid solution of calcium phosphate is neutralised with milk of lime, and gives a precipitate of calcium phosphate, which is used for making manures or as a source of phosphorus. A yield of bone fat is also obtained.

**Yield.**—100 parts of bones give 16 glue, 35 calcium phosphate precipitate, 8 fat.

The glue thus obtained is equal in every respect to hide glue. The acid, however, render the process somewhat expensive, consequently sulphurous acid



## A GELATINE LIQUOR INSTALLATION.

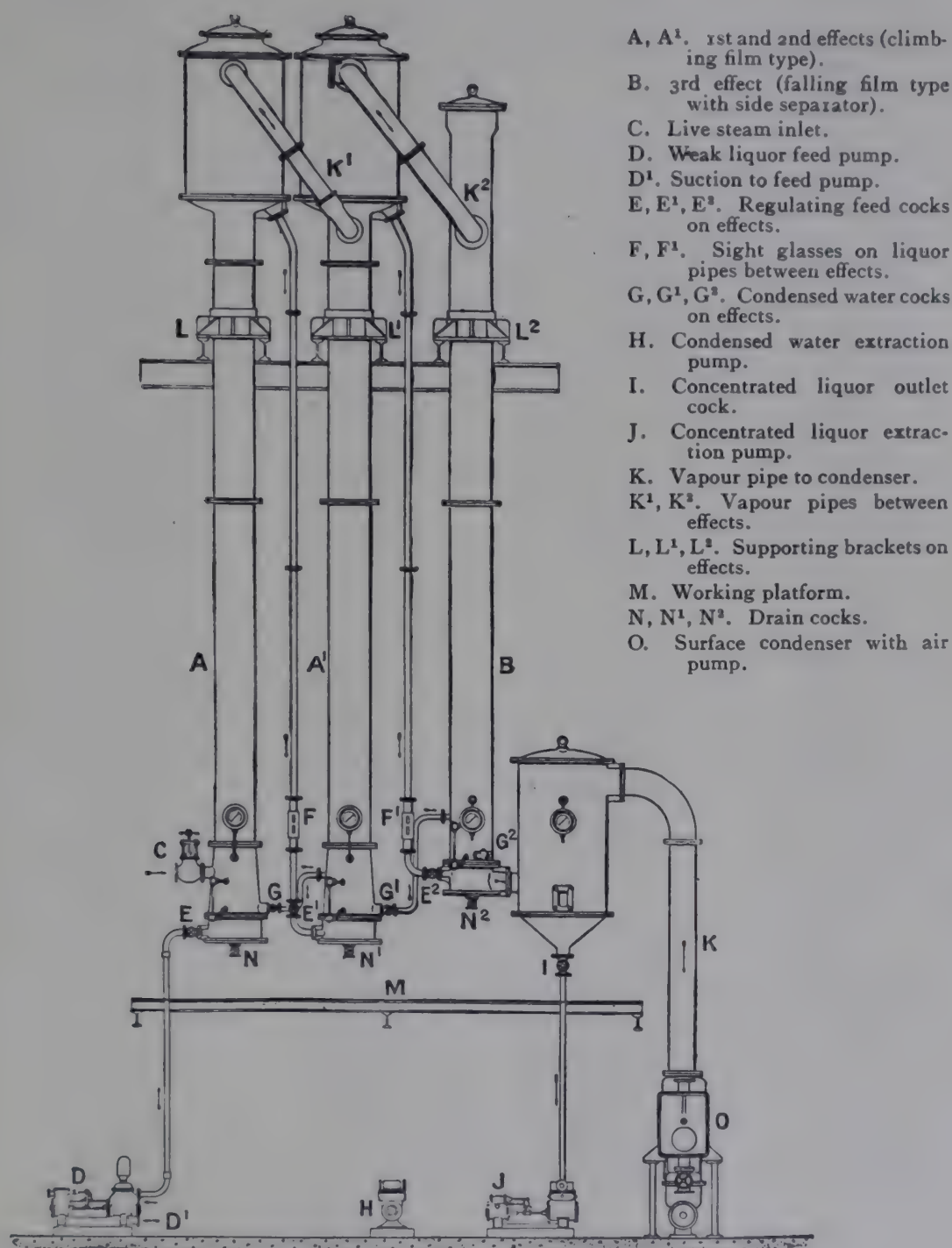


FIG. 238.—Kestner Triple Effect Evaporator for Gelatine Liquors.

Fig. 238 shows a diagram of a Kestner triple effect vacuum evaporator used for concentrating glue and gelatine liquors. A and A' represent ordinary climbing film evaporators, such as have been described under "Sugar" on page 157*a*. B represents a falling film evaporator, such as has been described under "Condensed Milk" on page 82.





*under pressure* has been used instead of HCl for extracting the mineral matter—a method which economises the acid and prevents the formation of an insoluble crust of calcium sulphite, which otherwise greatly retards solution.

Among other suggested improvements, German Patent, No. 166,904 purifies glue by dissolving it in warm  $\text{MgSO}_4$  solution and precipitating with HCl; German Patent, No. 168,872 uses monochloroacetic acid for extracting glue from bones, while German Patent, 177,625 uses dil. ammonia for the same purpose. German Patent, No. 187,261 bleaches glue by heating to  $100^\circ \text{C}$ . with the basic zinc salt of formaldehydesulphoxylic acid.

(b) The ordinary method is to first extract the bones with benzine or other solvent, thus obtaining the bone-fat (see under **Fats**). Steam is driven through the extracted bones to expel all solvent; the bones are then washed in rotating drums to cleanse them from dirt, flesh, etc. Next the bones are coarsely broken, placed in four iron cylinders and treated several times in succession with steam under 2 atmospheres pressure and with boiling water. The steaming has a disintegrating effect which renders the solution of the glue by the water more easy. When most of the nitrogenous matter has been extracted by the water, the bones (which should now contain less than 1 per cent. N) are ground up and used as manure (bone meal). The glue solutions are evaporated in vacuum pans as above described.

Since the mineral matter is closely united with the protein material of the bone, the glue is far more difficult to dissolve out from bones than from hides; consequently this kind of bone glue, which has been produced with a considerable amount of boiling, is not so good as the hide glue or the glue produced from bones by the acid process. Putrefying bones also yield an inferior product.

### Fish Glue

This is produced from fish scales and skins, also from fish heads and bones (especially cod) by treating with HCl, washing, liming, and boiling with water. The manufacture is carried out as with other glues, but alum is often used for decolourising. Isinglass is the purified and dried inner skin of the sturgeon's swimming bladder. Glue has been manufactured from whale blubber (German Patent 131,315) by extracting the oil first by cold pressing, then by extracting with benzol; the glutinous membrane remaining, dry and entirely fat-free, is then worked for glue.

Fish glue is used by cabinetmakers, and when properly made is as good as other kinds. Usually, however, it is deficient in adhesive power.

**Uses of Glue.**—Glue is used extremely widely for many very different industrial purposes, *e.g.*, for sizing special kinds of paper (drawing); in the hat industry; for finishing special kinds of woven material, especially silken netting; in joinery for cementing together wooden joints; in the printing industry for making printers' rollers, which consist of glue and glycerin or glue and treacle, forming an elastic, non-sticky and durable surface. In the colour industry paints are manufactured by rubbing up colouring matters with a solution of glue. In modelling and stuccato work a solution of glue is mixed with the plaster. "English Plaster"—used for wounds and cuts—consists of fine netting painted over with a solution of isinglass in alcohol. Cements for glass and porcelain usually consist of glue and mastic, or some similar resin, dissolved in alcohol. In the match industry very large amounts of glue are used as binding material.

**Testing Glue.**—The strength of a glue is usually tested by glueing pieces of dry clean wood together and ascertaining the force required to break the joint. Estimation of glue by precipitating with tannic acid is quite useless.

### Gelatine

Is a very pure colourless and odourless glue obtained either from calves' heads or the cartilage and skins of young animals, only the first extracts being used with the best sorts, and concentration by evaporation being avoided. The raw material must be quite fresh and very thoroughly cleansed; the glue solution is carefully clarified, being bleached with sulphurous acid. Gelatine for photographic purposes must be especially pure, since the slightest trace of putrefaction causes the generation of reducing compounds which act on silver or gold salts in the film. Such gelatine is prepared from the head and leg portions of calves, which are useless for leather manufacture; gelatine prepared from skin tissues has a great power of coagulation.



Gelatine is usually made in the form of very thin leaves (to facilitate rapid drying). They are frequently dyed with coal-tar colours; sugar and alcohol added make gelatine more flexible. Gelatine is now produced as threads, as a powder, and in thick plates.

**Uses.**—Gelatine is largely used as a food for making jellies, puddings, etc., for which purpose it is delicately coloured and mixed with sugar and flavouring materials. In photography it is largely used for preparing negatives, films, etc. Also for heliographical printing, the process depending upon the fact that if a plate covered with a mixture of gelatine and potassium dichromate is exposed to light, the illuminated portions become insoluble, while portions in the shade remain soluble; hence on washing the plate printable pictures are obtainable; formaldehyde also renders gelatine insoluble, and is used for making photographic films, vessels, ornaments, spangles for dresses, etc. The gelatine capsules used in medicine consist of gelatine and glycerol. In bacteriology gelatine is used as a transparent nutrition medium for cultivation. Fishing nets and sails are often coated with warm gelatine and then immersed in a concentrated solution of tannin, which renders the gelatine insoluble and preserves the fishing nets against the attacks of destructive organisms.

Gelatine is also used for removing turbidity from liquors such as beer and wine—which contain tannic acid. **Isinglass** (fish gelatine, consisting of the dried inner skins of the swimming bladder of the sturgeon and similar fish) is also much used for clearing and similar purposes, but is now being gradually displaced by gelatine.

Gelatine, isinglass, and other fish-bladder glues have only a very feeble adhesive power.

A vegetable gelatine is yielded by *Agar-agar*, a seaweed of the East Indies. It is nitrogen-free, consisting of carbohydrate.

**Glutol** or **Glutoform** is formaldehyde gelatine, prepared by evaporating a gelatine solution with formaldehyde or treating gelatine leaves with formaldehyde. Insoluble in hot water. Used as an antiseptic powder.

### Liquid Glue

When a solution of glue is mixed with acetic, nitric, or hydrochloric acid, or heated with zinc chloride, the glue still retains its power of sticking, but has lost its power of gelatinising. The following are some well-known receipts: 100 parts glue are dissolved in 110 parts boiling water, and 40 parts of nitric acid of 35° Bé. are added. 12 parts glue + 32 parts H<sub>2</sub>O + 2 parts HCl + 3 parts ZnSO<sub>4</sub>. Warm ten to twelve hours at 80°-85° C.

“**Liquid Glue**” is usually **dextrin** (which see) or of vegetable origin (see **Gum Arabic**, p. 346).

**Marine Glue** consists of india-rubber (1 part) dissolved in turpentine or paraffin (12 parts), to which are added 2 parts asphalt or shellac. A powerful waterproof adhesive; must be applied hot. Another recipe is: add 30 parts finely divided rubber to 2 parts melted tallow; melt carefully and stir in 2 parts lime or minium.

**Casein Cement** is made by mixing fat-free fresh casein (cheese) with milk of lime. It must be used immediately. It is a powerful cement much used by joiners, bookbinders, etc., also for cementing glass and porcelain (see **Industrial Casein**, p. 79).

For other adhesives, gums, etc., see under **Dextrin**, **Gum Arabic**, etc.

**Statistics.**—England imported in 1910 of glue, size, and gelatine, 246,500 cwt. (value £472,500); gluestock, 175,200 cwt. (value £120,120); isinglass, 10,400 cwt. (value £109,800).

The glue export amounted to 300,300 cwt. (value £242,500).

The yearly sale of glue in the United States amounts to about \$12,000,000. The United States imported in 1910 73,400 cwt. of glue (value \$862,000); gluestock of value \$1,605,000; gelatine, 11,100 cwt. (value \$387,000); isinglass, 3,000 cwt. (value \$76,000).

The United States export of glue was 28,200 cwt. (value \$299,000) in 1906, and 22,200 cwt. (value \$262,000) in 1910.

For modern statistics see Appendix III.



# INDUSTRIAL ALBUMEN

## LITERATURE

RUPRECHT.—“Die Fabrikation von Albumen und Eierkonserven.” Vienna, 1904.

GEOFFREY MARTIN.—“The Lecithin and Albumin Industry.” *Chemical World*, 1913, 2, 47.

Two varieties of albumen are now on the market, viz., egg albumen and that derived from blood serum. They have different properties.

## Egg Albumen

The approximate composition of egg albumen is: Water, 84 per cent.; dry albumen, 11.9; fats, etc., 3.6; ash, 0.5 per cent.

**Properties.**—Egg albumen coagulates at 72°-73° C. In a 1 per cent. solution albumen coagulates at 56° C. The sp. gr. is 1.0026 for a 1 per cent. albumen solution, and 1.0515 for a 15 per cent. Albumen is precipitated from solution by alcohol, tannic acid or tannin, lead acetate, metaphosphoric acid, etc.

Albumen combines with acids to produce acid albumens, and with bases to produce alkali albumens. It also unites with halogens—in fact it is a very reactive substance. All these compounds are unstable.

When dried, albumen will keep almost indefinitely. Moist albumen soon putrefies.

**Manufacture.**—The eggs are broken, separated from the yellow yolk without mixing, the albumen strained through silk gauze lining the lead-lined drums of centrifugal machines, allowed to settle for thirty to forty hours (or cooled five to six days to a low temperature in iron vessels), when the albumen should be quite clear. Some firms clarify by a little tannin or acetic acid and turpentine oil and pressure through a Vollmersch filtering apparatus. The clear albumen is then dried as rapidly as possible in a stream of dry air or *in vacuo* (see Fig. 21, p. 81, in **Condensed Milk**) under 50° C. (above this temperature the albumen becomes yellow) for about four to six hours, when it is obtained as thin clear elastic sheets; 230-300 eggs yield 1 kg. dry albumen. With water it dissolves to a perfectly clear odourless solution.

**Industrial Lecithin** (yolk powders) is made from the egg yolks above separated. The Lecithin forms a pasty mass which is absorbed in wheat protein, and sold as a component of invalid foods and for other purposes. **Lecithin** is a compound of **choline**, **glycerol**, **phosphoric** and various fatty acids, and occurs in the brain-substance, bile, and blood. It has great medicinal value. For methods of extraction see *German Patents*, Nos. 200,253, 210,013, 223,593, and *French Patents*, Nos. 371,391, 390,683.

## Blood Albumen

The freshly caught blood is spread in shallow dishes and when the separation into fibrin and pale yellow serum is complete, the latter is treated like egg albumen (above). To obtain the albumen quite pure the serum is forced through charcoal filters, the albumen precipitated with lead acetate, washed, and the lead albuminate decomposed with CO<sub>2</sub>, settled, the lead removed by H<sub>2</sub>S and filtered, and the albumen evaporated *in vacuo* as above described. 1 kg. serum albumen requires the blood of 2.5 cows, 10 sheep, or 17 calves. For various improvements see English Patent 10,227, 1905, and German Patents 137,994, 143,042.

**Uses.**—As a mordant in dyeing and calico printing; in the manufacture of gums and adhesives; as a clarifying agent; for the preparation of photographic papers; in medical foods.

**Statistics.**—The German import in dried albumen amounted in 1910 to 612 tons, in value £125,000: the majority came from China. The English import in 1910 amounted to £21,767.

The United States in 1910 imported 88 tons (value \$29,000) of blood albumen; 312 tons (value \$269,000) of egg albumen; and 3½ tons of unspecified albumen (value, \$1,200).

For modern statistics see Appendix III.





## SECTION XXI

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The Industry of Modern Synthetic and  
other Drugs





# THE INDUSTRY OF MODERN SYNTHETIC DRUGS

Originally written by F. CHALLENGER, Ph.D., B.Sc.  
Revised by E. I. COOKE, M.A.(Cantab.), B.Sc., A.R.I.C.

## LITERATURE

### MERCK'S ANNUAL REPORTS.

WAUGH, ABBOTT, AND EPPSTEIN.—"Alkaloidal Therapeutics." Chicago, 1907.

KEANE.—*Journ. Soc. Chem. Ind.*, 15th April 1910, 388.

MARTINDALE AND WESTCOTT.—"Salvarsan (606)." London, 1911.

" " —"The Extra Pharmacopœia." 2 vols. London.

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JOWETT AND PYMAN.—"Relation between Chemical Constitution and Physiological Action." *Proc. Internat. Congress of Applied Chemistry*, 1909, Sect. IV. A, I.

GARRATT.—"Drugs and Galenicals." Chapman & Hall.

KENDALL.—"Thyroxine." Chapman & Hall.

CHAIN.—"Chemical Properties and Structure of Penicillin: Endeavour," 7, No. 27, July 1948; 7, No. 28, October 1948.

NISBET.—"Anæsthetics." The Royal Institute of Chemistry, 1948.

DALE.—"Chemistry and Medicinal Treatment." Third Dalton Lecture. Royal Institute of Chemistry, 1948.

The following works deal with natural alkaloids:—

WINTERSTEIN U. TRIER.—"Die Alkaloide." Berlin, 1910.

PICTET.—"Die Pflanzenalkaloide und Ihre Chemische Konstitution." Berlin, 1900.

BRÜHL, HJELT, U. ASCHAN.—"Die Pflanzenalkaloide." Braunschweig, 1900.

J. SCHMIDT.—"Pflanzenalkaloide (Konstitution u. Synthese)." Stuttgart, 1900.

" " —"Die Alkaloidchemie in den Jahren 1900-1911." 3 vols.

For **Trade Names** of the newer drugs, see list on p. 677 (Appendix II).

## INTRODUCTION

It is impossible in the space at our disposal to give a complete account of the enormous number of new drugs now on the market. The reader is referred to the above-mentioned literature for further information. All that is attempted is a brief account of some of the more important of the drugs—especially the newer synthetic ones—which within the last few years have been placed on the market, and which will in the future play an important part in therapeutics.

The larger modern chemical firms—such as Burroughs Wellcome & Co.; I.C.I. Pharmaceuticals; May & Baker; Merck; Meister, Lucius, & Brüning—employ a staff of university-trained scientists to synthesise and test new drugs, and some of the recent discoveries made by

these firms are certainly epoch making. The whole chemistry of **Ergot**, for example, was revolutionised by work carried out in the laboratories of Messrs Burroughs Wellcome & Co. by Barger and others, while equally important work has been done by Meister, Lucius, & Brüning, of Höchst, on **Adrenaline** and on the organic arsenic compounds used in treating sleeping sickness and syphilis. Still more recently, exemplary chemotherapeutic research, including co-ordinated chemical and biological investigations by the staff of the research department of I.C.I. Pharmaceuticals of Blackley, resulted in the synthesis of the new antimalarial drug **Paludrine**. The isolation of **Penicillin**, timed to save many lives in the 1939-1945 war, is another landmark in the history of modern synthetic drugs.

**Statistics.**—The following figures show the magnitude of the import and export of drugs into the United Kingdom :—

IMPORT.

	1906.	1913.	Value, 1913.
Opium - - - - -	825,836 lbs.	566,834 lbs.	£507,261
Quinine and quinine salts- - - - -	1,973,039 oz.	2,422,944 oz.	102,101
Peruvian bark - - - - -	24,602 cwt.	26,122 cwt.	58,000
Chloral hydrate - - - - -	19,978 lbs.	23,501 lbs.	2,080
Chloroform - - - - -	972 „	1,366 „	347
Other drugs and medical preparations -	...	...	1,302,800
Total - - - - -	...	...	£1,972,589

The amount of imported tea for the manufacture of **caffeine** was 1,500,000 lbs. (value £10,300) in 1913.

EXPORT.

	1906.	1913.	Value, 1913.
Cocaine - - - - -	...	3,300 oz.	£1,000
Morphia - - - - -	...	400,000 „	193,000
Opium - - - - -	...	12,100 lbs.	12,400
Quinine and quinine salts - - - - -	1,059,948 oz.	1,374,000 oz.	72,600
Other medicines and drugs - - - - -	...	...	2,072,000

The United States imports (entered for consumption) in 1910 were :—

	Quantity.	Value.
Caffeine - - - - -	60,500 lbs.	\$100,500
Chloroform - - - - -	960 „	1,500
Cinchona bark - - - - -	3,300,000 „	242,000
Quinine sulphate, quinine, and other alka- loids from cinchona bark - - - - -	3,000,000 oz.	398,000
Cocaine - - - - -	29,600 „	38,000
Cocaine salts, ecgonine - - - - -	24,900 „	42,000
Ergot - - - - -	181,600 lbs.	53,000
Ichthyol - - - - -	14,400 „	21,500
Iodoform - - - - -	31 „	97
Opium - - - - -	439,000 „	1,575,000
Morphia and salts - - - - -	13,000 oz.	60,000
Other opium alkaloids - - - - -	23,000 „	66,000
Santonin and salts - - - - -	7,300 lbs.	53,000
Strychnine and salts - - - - -	2,000 oz.	1,000

For modern statistics see Appendix III.



## ANÆSTHETICS

**Anæsthetics** may be divided into (a) General Anæsthetics (including Basal Anæsthetics), (b) Local Anæsthetics.

## (a) General Anæsthetics

Produce total insensibility to pain. Usually administered by inhalation. The most important are:—

**Chloroform**,  $\text{CHCl}_3$ .—For manufacture and properties see p. 377. For anæsthetic purposes it should contain 1 per cent. absolute alcohol, or it undergoes decomposition. Used for operations where a considerable interval of anæsthesia is required.

**Ether**,  $\text{C}_2\text{H}_5\text{O.C}_2\text{H}_5$ .—For preparation and properties see p. 381. Ether gives a shorter period of anæsthesia than chloroform.

**Ethyl Chloride**,  $\text{C}_2\text{H}_5\text{Cl}$ .—Obtained by passing dry  $\text{HCl}$  gas into ethyl alcohol in the presence of  $\text{ZnCl}_2$  (see p. 377). B.P.  $12.5^\circ \text{C}$ ., hence is gaseous at ordinary temperatures. Miscible with alcohol. Sparingly soluble in  $\text{H}_2\text{O}$ . Produces anæsthesia in 30 to 120 seconds, which endures for fifteen to twenty minutes. Only one-nineteenth the paralysing action on the heart of that possessed by chloroform.

**Ethyl Bromide**,  $\text{C}_2\text{H}_5\text{Br}$ .—Now produced very pure by Merck. Colourless liquid of B.P.  $38.4^\circ \text{C}$ .; sp. gr. ( $13^\circ \text{C}$ .) 1.47. Produces extremely rapid anæsthesia, but has a somewhat irritating action on the lungs.

**Narcotil** is a mixture of methyl and ethyl chlorides.

**Somnoform** consists of the same ingredients with the addition of **ethyl bromide**.

**Nitrous Oxide**,  $\text{N}_2\text{O}$ , were it more potent would qualify as the ideal anæsthetic. It is non-toxic and more pleasant to take than ether. Sickness and lung irritation are rarely observed with this anæsthetic. Nitrous oxide is safer than chloroform but unfortunately much less powerful. Consequently it must be used in a ratio of 90 : 10 or 95 : 5 with oxygen. Owing to the small proportion of oxygen present, nitrous oxide can only be used for operations lasting from  $\frac{1}{2}$  to  $1\frac{1}{2}$  minutes.

Nitrous oxide is a colourless gas with a sweetish taste and odour. It has a boiling-point of  $-88^\circ \text{C}$ . and a critical temperature of  $36^\circ \text{C}$ . and can thus be liquefied by pressure alone.

**Cyclopropane**,  $\begin{array}{c} \text{CH}_2 \\ \diagup \quad \diagdown \\ \text{CH}_2 - \text{CH}_2 \end{array}$ , is prepared by the action of zinc dust on an alcoholic solution of 1 : 3-dibromopropane. It is a gas at ordinary temperatures, has a boiling-point of  $-34^\circ \text{C}$ . and a melting-point of  $-126.6^\circ \text{C}$ .

Cyclopropane has become one of the most used anæsthetics. It was discovered by Lucas, Henderson, and Brown of Toronto. First clinical tests were

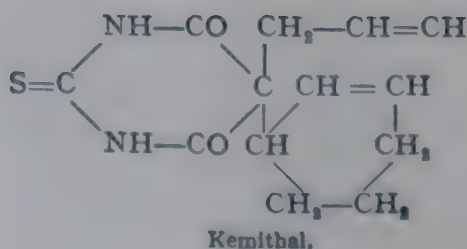
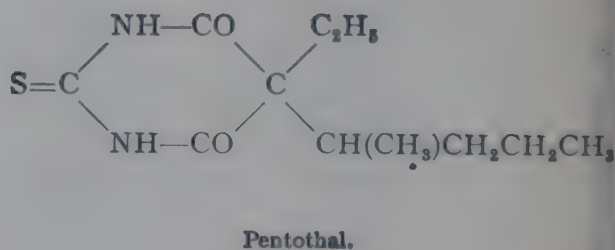
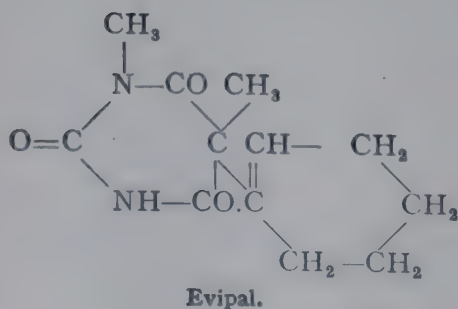
conducted by Dr R. M. Waters in the University of Wisconsin in 1930. The gas is one of the most potent of the inhalant anæsthetics. When premedicated with morphia a concentration of only 13 per cent. produces full anæsthesia. The toxic concentration is about 43 per cent. so that a wide margin of safety can be maintained. Induction is rapid and pleasant and unconsciousness is reached after about  $1\frac{1}{2}$  minutes. Care must be taken with this anæsthetic as the transition from the induction stage to complete anæsthesia is very rapid. The rhythm of the heart is affected before that of respiration, but when premedication with barbiturates is practised the respiration is affected first. Cyclopropane does not affect the kidneys or the liver. Mallinson, *Lancet*, 1945, 249, 75, states that the best results with cyclopropane are obtained when induction is brought about by means of pentothal, plane (2) anæsthesia maintained with cyclopropane and curare injected at the amount of 1 mg./kg. body-weight to induce muscular relaxation.

**Basal Anæsthetics.**—A group of anæsthetics known as basal anæsthetics are certain solids or liquids which can be administered in solution intravenously or rectally, *e.g.*, evipan (or evipal), pentothal, paraldehyde, and avertin. Pentothal is now used as a general anæsthetic. A few examples of basal anæsthetics are now given:

**Tribromoethanol-*tert.* amyl alcohol.**—Willstätter and Duisberg prepared this compound in 1923, and in 1926 Duisberg introduced it as an anæsthetic. Freshly dissolved in *tert.* amyl alcohol it constitutes the anæsthetic **Avertin-fluid**. When administered rectally it is rapidly absorbed from the colon and the small intestine. As the dose for satisfactory surgical anæsthesia is rather above the recommended dose avertin is only used for the lighter operations. It is often combined with regional or inhalent anæsthetics for the heavier ones.

**Paraldehyde** is used in a similar way to avertin, but nowadays it is generally regarded as an hypnotic.

**The Barbiturates.**—Three examples of these now well-known materials will be given: **Evipal** (hexobarbitone), **Pentothal**, and **Kemithal**.





These drugs may be used for the following purposes:—

- (a) As induction agents.
- (b) As basal anæsthetics.
- (c) For producing total anæsthesia for both short and long operations.

The above drugs are usually administered intravenously but may also be administered rectally and intramuscularly. After intravenous injection the barbiturates remain in the blood for only a short time. In general the drugs are eliminated by destruction in the liver and by excretion by the kidneys. It has been shown that pentothal remains in the blood and tissues for a very short time, but that the depression caused by the drug lasts for a long time. Kemithal is only half as potent as pentothal and slightly less active than evipal. There is less danger to the respiration with kemithal than when using pentothal. It is almost completely destroyed in the body and there is no protracted post-operative depression. It has been said that the barbiturates give a form of anæsthesia most resembling that of natural sleep.

### (b) Local Anæsthetics

There is a large and increasing number of organic compounds which, under suitable conditions, can render certain definite portions of the body insensible to pain ("local anæsthesia"). Certain alkaloids, for example, when dropped upon the eye in the form of solution, render possible operations which would otherwise have to be performed under the influence of chloroform or one of the other general anæsthetics. Similarly, when such a substance is injected at the base of the spine, the whole of the region of the loins is rendered completely insensible to pain.

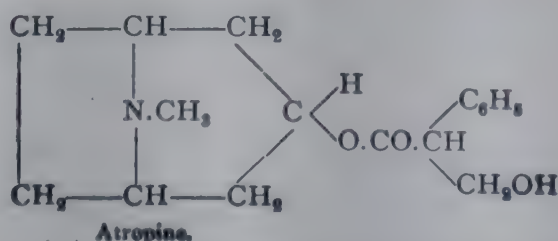
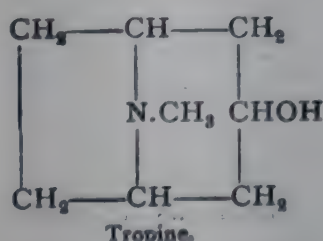
The discovery of the action of these drugs is one of the very greatest importance to the medical man, and during the last ten years they have almost superseded chloroform for the performance of several of the less serious operations. Moreover, in cases where, for several reasons, it is not yet considered advisable to dispense with the use of a general anæsthetic, the quantity of the latter which is required has been considerably reduced by administering a local anæsthetic as well. This is of special importance in cases where, owing to certain diseased conditions of the organism, the use of chloroform is attended with more than the usual amount of danger.

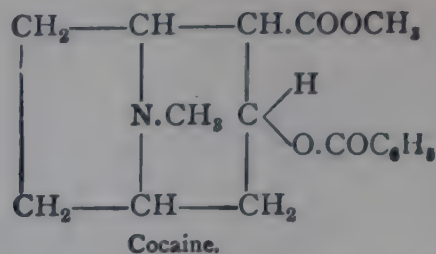
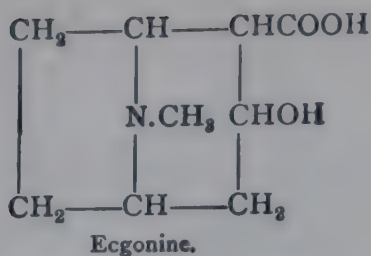
Most of these drugs are administered by injection into the region which it is desired to anæsthetise. For operations upon the eye, the solution is usually applied in the form of drops.

The chief local anæsthetics employed are:

**Cocaine**,  $C_{17}H_{21}NO_4$ , a white crystalline alkaloid occurring in the leaves of *Erythroxylon coca* of Bolivia and Peru. The leaves contain 1 per cent. ether soluble alkaloids, about half of which is cocaine, the other alkaloids including tropacocaine, truxilline, cinnamylcocaine, and hygrine. The leaves are exhausted with water at  $60^{\circ}$ – $80^{\circ}$  C., protein matter precipitated with lead acetate, excess of lead removed by  $Na_2SO_4$ , the filtered solution concentrated, made alkaline with ammonia, and the alkaloid extracted with ether.

Cocaine is methylbenzoylecgonine, ecgonine being a carboxyl derivative of tropine. Its relationship to atropine, the alkaloid of *Atropa belladonna* or the Deadly Nightshade, will be seen from the constitutional formulæ:





Other alkaloids, with very undesirable action, which occur in the coca leaves, may be converted into ecgonine by heating with HCl. Pure cocaine can then be prepared synthetically from ecgonine.

**Properties.**—Large colourless crystals, M.P.  $98^\circ \text{C}$ .; bitter taste; very sparingly soluble in water; soluble in alcohol, ether, benzene, chloroform, etc. Forms monovalent salts with acids.

In small doses the drug sustains muscular energy, raises the body temperature and blood pressure. Dilates the eye pupil. Excess causes death by convulsions. Its chief value is its power of paralysing nerve-ends, and so causing local anæsthesia for minor surgical operations. Maximum daily dose, 0.15 g.; maximum single dose, 0.05 g. For injections a 5-10 per cent. solution is used.

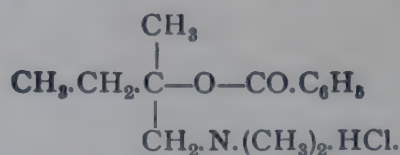
**Tropacocaine** = benzoyl- $\psi$ -tropine,  $\text{C}_{15}\text{N}_{19}\text{NO}_2$ . Accompanies cocaine in the leaves of *Erythroxylon coca*; sixty-three times less toxic than cocaine, and its action commences more quickly. No dilation of the pupil. It is an excellent local anæsthetic, and is coming more and more into use.

Synthetic substitutes for cocaine are:—

**Anæsthesine**,  $\text{NH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{COOC}_2\text{H}_5$ .—Obtained by reducing *p*-nitrobenzoic ethyl ester with Sn + HCl. Excellent anæsthetic of low toxicity and non-irritant power. Used for anæsthisng wounds and checking vomiting.

**Novocaine**,  $\text{NH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{N}(\text{C}_2\text{H}_5)_2 \cdot \text{HCl}$ .—Excellent local anæsthetic, used in dentistry, and for the production of spinal anæsthesia. Often used with adrenaline.

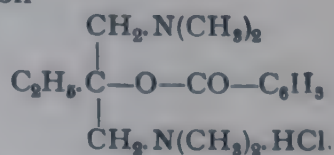
**Stovaine** forms white, lustrous scales, M.P.  $175^\circ$ , readily soluble in water; prepared by the interaction of magnesium ethyl bromide and dimethylaminoacetone, and subsequent benzylation of the product thus formed. It has the constitution:—



As little as 0.3 c.c. of a 10 per cent. solution are sufficient to produce anæsthesia in the legs below the knees.

Much used as a local anæsthetic in dental, ophthalmic, and minor surgical operations. Much less toxic than cocaine.

**Alypine** has the constitution



Readily soluble in  $\text{H}_2\text{O}$  and probably superior to stovaine as a local anæsthetic. Used as a substitute for cocaine in 1-5 per cent. solution.

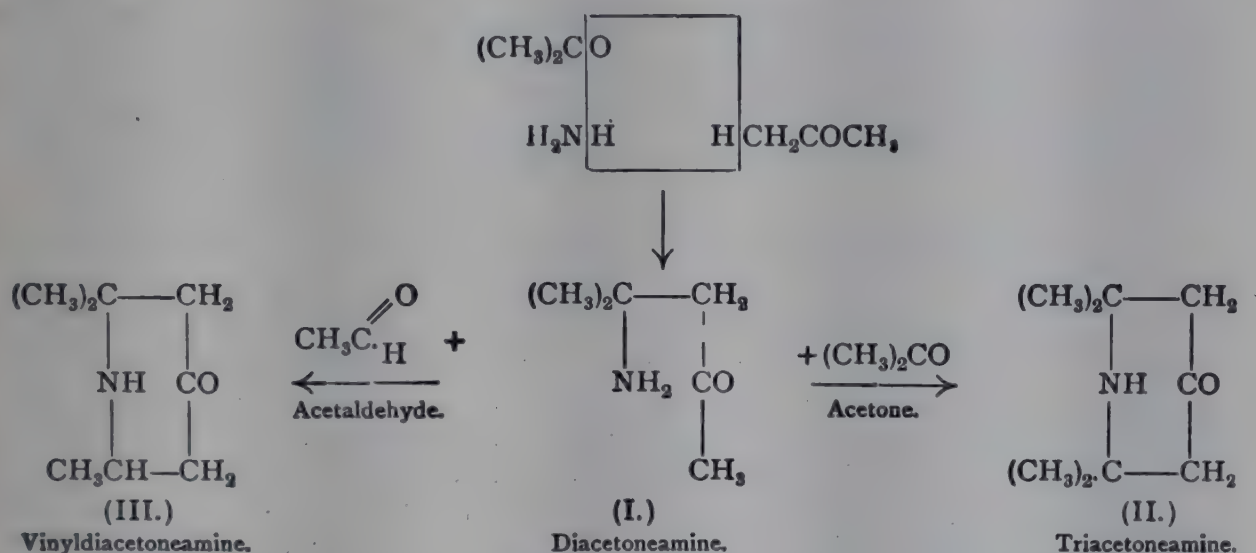


When administered along with heroine (diacetylmorphine) the demulcent and sedative effects of the latter drug are enhanced, and the combination has proved very successful in allaying the nocturnal cough of pulmonary tuberculosis.\*

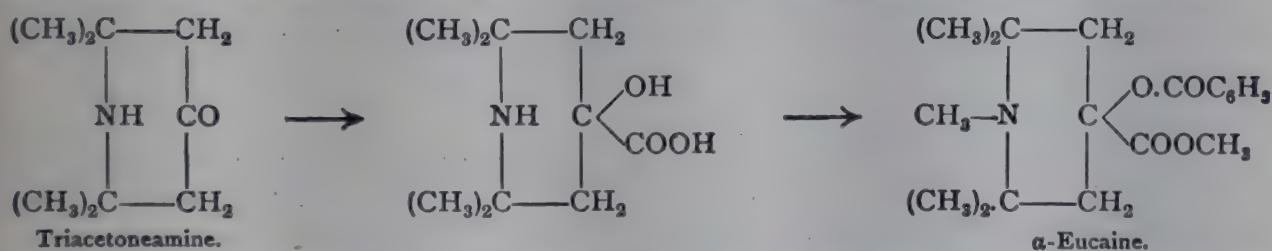
**The Eucaines.**—The important results which usually follow the determination of the chemical constitution of any important physiologically active substance are well instanced by the existence of  $\alpha$ - and  $\beta$ -eucaine.

The preparation of these two compounds was a direct outcome of the various attempts which were made to prepare substances chemically related to cocaine.

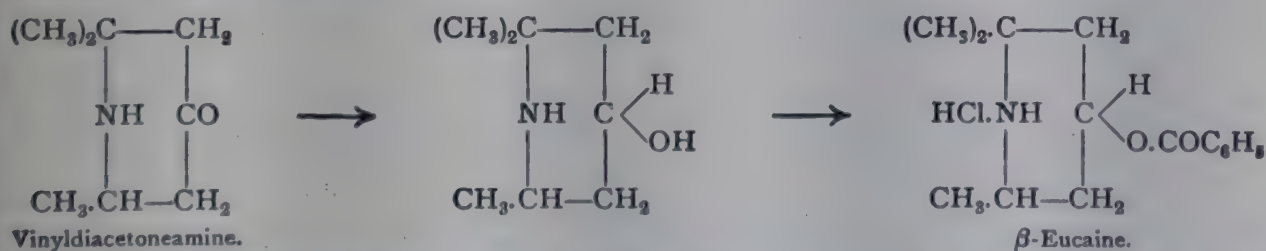
**Preparation of the Eucaines.**—By the condensation of 2 molecules of acetone with 1 of ammonia, diacetoneamine is formed (I.). If this be allowed to react with a third molecule of acetone, the symmetrical triacetoneamine is obtained (II.). If instead of allowing the diacetoneamine to react with acetone, acetaldehyde be used, the product is a substance known as vinyl diacetoneamine (III.). Thus:—



**Triacetoneamine** is a crystalline solid, M.P.  $39^\circ$ - $40^\circ$ . It has a strong alkaline reaction and its odour is ammoniacal, and also similar to that of camphor. When converted into its cyanhydrin, and then hydrolysed, methylation and benzylation of the resulting hydroxy acid yield  $\alpha$ -eucaine.



**Vinyl diacetoneamine** is a volatile base, M.P.  $27^\circ$ , B.P.  $200^\circ$ , which forms salts with acids. When the carbonyl group in this substance is reduced, benzylation yields a derivative, the hydrochloride of which is  $\beta$ -eucaine.



$\alpha$ - and  $\beta$ -eucaine are colourless crystals, the former soluble in 10 parts and the latter in 30 of water.  $\alpha$ -Eucaine has been abandoned in practice owing to its irritant action on the tissues.

The anæsthetic action of  $\beta$ -eucaine is somewhat feeble than that of cocaine, and in consequence of its vasodilatory properties it gives rise to hæmorrhage and causes pain when injected. It has also a tendency, when used in ophthalmic surgery, to cause hardening. This difficulty seems to have

\* Laufer, "Merck's Reports," 1907, 21; *Reichs-Medizinal-Anzeiger*, 1907, 17.



been largely overcome by Langgaard \* by combining  $\beta$ -eucaine with lactic acid, when a product is obtained which is non-irritant and causes neither local anæmia, hyperæmia, nor shrinkage. Injections of  $\beta$ -eucaine have been employed by Opitz† with very great success in the treatment of sciatica and neuralgia, the drug having a decided curative as well as analgesic effect.

In spite of the similarity in chemical constitution between the eucaines and cocaine, they are hardly such satisfactory substitutes for the latter drug as tropacocaine.

## SYNTHETIC ANTIPYRETICS

**Acetanilide, or Antifebrin**,  $C_6H_5.NH.COCH_3$ , prepared by heating in earthenware vessels for one to two days equal parts of aniline and glacial acetic acid :  
 $C_6H_5.NH_2 + CH_3.COOH = H_2O + C_6H_5.NH.CO.CH_3$ .

Used as a febrifuge in cases of typhoid fever, small-pox, phthisis, rheumatism, and erysipelas. Prolonged use is dangerous.

**Acetylsalicylic Acid (Aspirin)**,  $C_6H_4(CO_2.CH_3).CO_2H$ , prepared by heating salicylic acid with acetic anhydride or acetyl chloride, and recrystallising from chloroform. See also American Patent 749,980 and English Patent 15,517/02. White needles, M.P.  $135^\circ$ . Moderately soluble in water, easily in alcohol and ether. Dose, 0.5 g. ; 4 g. may be given daily for rheumatism and neuralgia.

**Phenacetine** is acetyl *p*-phenetidine,  $C_6H_4 \begin{matrix} \swarrow O.C_2H_5 \\ \searrow NH.CO.CH_3 \end{matrix}$ . *Preparation.*—

Phenol,  $C_6H_5OH$ , is nitrated, and the *p*-nitro-phenol,  $C_6H_4.(NO_2).OH$ , is separated from the *o*-compound, and ethylated with ethyl sulphate, whereby  $C_6H_4.(NO_2).OC_2H_5$  is produced. This is reduced with  $Sn + HCl$ , thereby producing **Phenetidine**,  $C_6H_4.(NH_2).OC_2H_5$ , which is then acetylated by boiling with acetic acid, thus producing phenacetine,  $C_6H_4.(OC_2H_5).NHCOCH_3$ . White crystals; tasteless; valuable antipyretic and antineuralgic. Dose, 0.5-0.75 g. Very largely used, England importing about  $8\frac{1}{2}$  tons yearly. Owing to its sparingly soluble nature its action takes place slowly. This defect is partially overcome by introducing an  $NH_2$  group into its acetyl group, thus producing **Phenocoll**.

**Triphenine** is propionyl-*p*-phenetidine,  $C_6H_4(OC_2H_5)NH(CO.CH_2.CH_3)$ , prepared similarly to phenacetine by heating *p*-phenetidine with propionic acid. Very sparingly soluble in  $H_2O$ . M.P.  $120^\circ C$ . Antipyretic and antineuralgic.

**Phenocoll**,  $C_6H_4(OC_2H_5).NH.CO.CH_2.NH_2$ .—It is prepared by acting on phenetidine with chloracetyl chloride, and treating the resulting compound with ammonia; its salts are soluble in water. It is a rapidly acting antipyretic and antineuralgic, but is transitory in its effects.

**Neraltein**, a new drug, is the sodium salt of *p*-ethoxyphenylaminomethanesulphonic acid; white crystals, soluble in 10 parts of cold water.



Only slightly toxic, and in small doses produces no irritation of the kidneys; possesses good analgesic properties, and has been used in slight cases of rheumatism.

**Antipyrine** is the most important member of the "pyrazolone drugs."

**Manufacture.**—Phenylhydrazine (II.) (216 parts) is dissolved in dilute sulphuric acid (300 g. of acid in 2 l. of water). Ethyl acetoacetate (I.) (260 parts) is then allowed to flow into the solution at a temperature of about  $40^\circ$ , the mixture being stirred constantly. After the reaction is at an end, excess of caustic soda solution is added and the mixture extracted with ether. From the ethereal extract, after washing with caustic soda solution and drying over calcium chloride, methyl-phenyl-pyrazolone (III.) is obtained as an oil which can be distilled *in vacuo*.

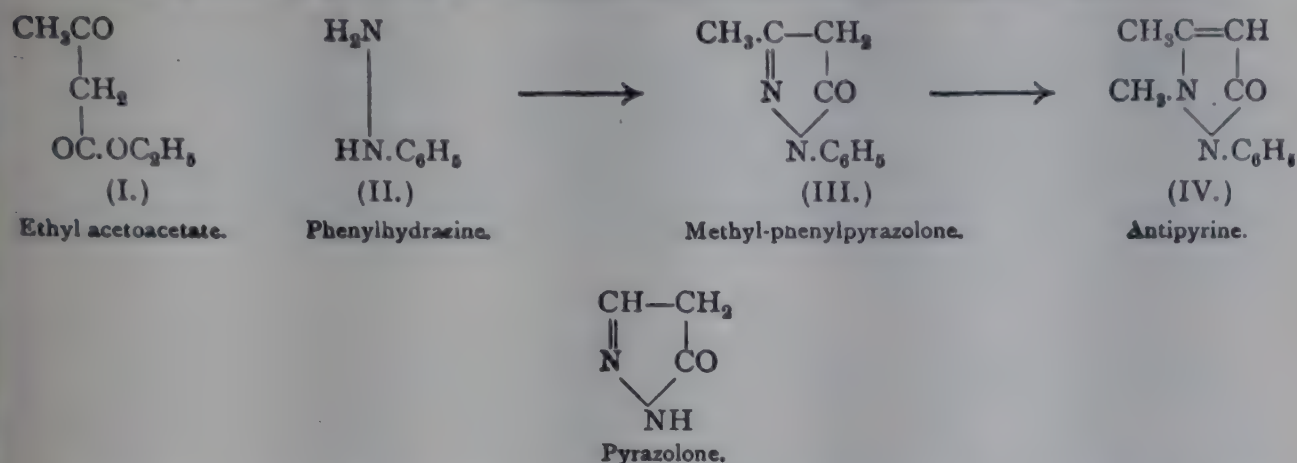
When 200 parts of this are heated with 140 parts of methyl iodide and 200 parts of methyl alcohol at  $100^\circ$ - $110^\circ$  for twelve hours, methylation takes place. After removing the alcohol by evaporation

\* "Merck's Reports," 1904, 63; *Therapeutische Monatshefte*, 1904, No. 8, 416.

† *Ibid.* 1907, 97; *Klinisch-therapeutische-Wochenschrift*, 1907, No. 14.



the residue is decolourised with a little dilute solution of sulphurous acid. Caustic soda is then added and the precipitated oil extracted with benzene from which solvent the drug can be crystallised.



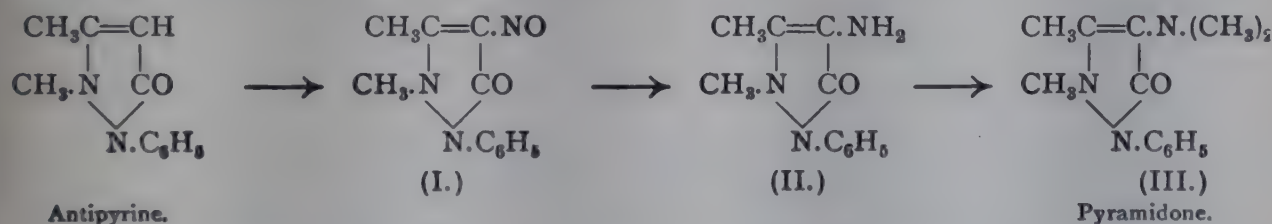
Antipyrine (IV.) forms colourless, inodorous, scaly crystals possessing a bitter taste; readily soluble in water, chloroform, or alcohol. M.P.  $112^\circ-113^\circ$ . Acts as a base forming salts directly with acids. Much valued for the treatment of fever, neuralgia, and rheumatism. Dose, 0.25-2 g. daily.

Tussol—prescribed for whooping cough—is the antipyrine salt of Mandelic acid.

Migräneine is a mixture of caffeine citrate and antipyrine, used for headaches, etc., as an antipyretic and antineuralgic.

Salipyrine is antipyrine salicylate.

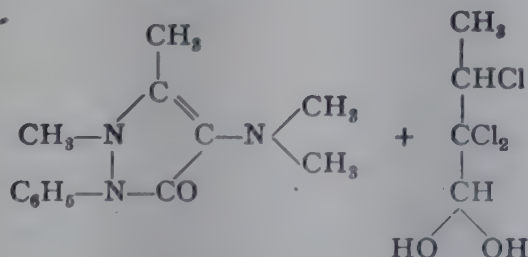
Pyramidone, 4-dimethylamino-antipyrine, is prepared from antipyrine hydrochloride by the action of nitrous acid whereby a nitroso-antipyrine is produced (I.). On reduction this is converted into aminoantipyrine (II.) which is isolated in the form of its benzylidene derivative. On treatment with methyl iodide it yields pyramidone (III.). This forms small colourless crystals of slightly bitter taste which are readily soluble in water. M.P.  $108^\circ$ .



Pyramidone possesses advantage over antipyrine in that it may be prescribed in cases where there is cardiac weakness. The effective dose is only one-third that of antipyrine while it has no irritant effect on the stomach or kidneys.

It has been largely used to allay the high temperatures of typhoid fever and of phthisis, and also in neuralgia and rheumatism.

Trigemine is dimethylaminoantipyrine + butyl chloral hydrate,  $\text{C}_{17}\text{H}_{24}\text{O}_8\text{N}_3\text{Cl}_3$ ,  
or :—



It is prepared by mixing dimethylaminoantipyrine with butyl chloral hydrate. M.P.  $85^\circ$ . Soluble in  $\text{H}_2\text{O}$ , alcohol, and benzene; less so in ether and ligroin. Has an analgesic effect, and is prescribed for headaches, neuralgia, etc. Mild antipyretic. Dose, 0.5-1.2 g.

## HYPNOTICS

An ideal hypnotic will produce a normal sleep as differentiated from a **narcotic** which produces unconsciousness by intoxication.

The first hypnotic used was **Chloral Hydrate**,  $\text{CCl}_3\cdot\text{CH}(\text{OH})_2$  (1869), the manufacture and properties of which are treated on p. 379. Chloral hydrate, while producing sleep, exerts a depressing action on the heart, sometimes acts as a toxic agent, and often sets up the "chloral habit." Consequently a large number of substitutes have been sought.

**Dormiole** is amylene chloral,  $\text{CCl}_3\cdot\text{CH}(\text{OH})\cdot\text{O}\cdot\text{C}_5\text{H}_{11}$ , produced by mixing 6 parts amylene hydrate + 10 of chloral. Colourless oily liquid, insoluble in water, soluble in alcohol, ether, acetone, etc. Useful and harmless soporific in **heart disease** and **nervous troubles**, etc.

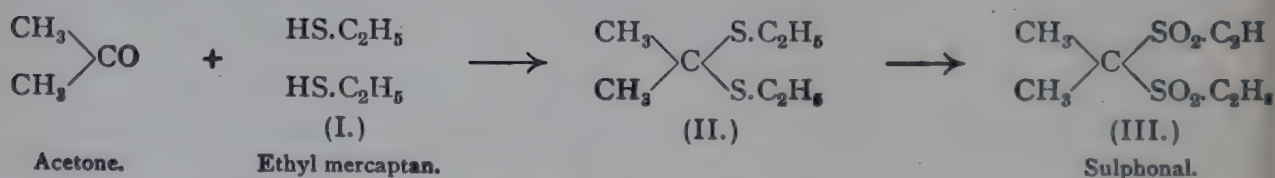
**Isopral** is trichlorisopropyl alcohol,  $\text{CCl}_3\cdot\text{CH}(\text{OH})\cdot\text{CH}_3$ , prepared by treating chloral with methyl magnesium iodide and decomposing with dilute acid—



Colourless crystals, M.P.  $49^\circ\text{C}$ ., soluble in alcohol, ether; sparingly soluble in  $\text{H}_2\text{O}$ . Twice as powerful hypnotic as chloral hydrate. Dose, 0.5 to 1 g. In insanity, 2-3 g.

**Acetone Chloroform, Chloretone**,  $(\text{CH}_3)_2\text{C}(\text{OH})\cdot\text{CCl}_3$ , is used as a soporific, inhalation anæsthetic, and a remedy for sea-sickness.

**Sulphonal**, diethylsulphonedimethylmethane (III.), is prepared by condensing acetone with ethyl mercaptan (I.) and oxidising the resulting compound (II.) with potassium permanganate.



Heavy, colourless prismatic crystals, M.P.  $125.5^\circ$ , soluble in 500 parts of water, 133 parts of ether, and 65 parts of alcohol at  $15^\circ\text{C}$ ., and in 15 parts of boiling water. It should be free from odour. Used as a sleep producer (dose, 10-20 gr. = 0.65-1.3 g.), also prescribed in epilepsy and in diminishing the sweats of phthisis.

Single, occasional doses do not affect the health, but the continued administration of the drug has been known to lead to serious consequences, such as mental confusion, difficulty of speech and breathing, paralysis of the legs, and finally death.

**Trional** and **Tetronal** are two drugs closely allied to sulphonal. Their constitution is shown below :—



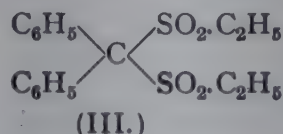
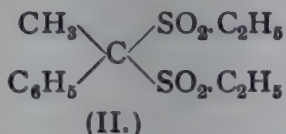
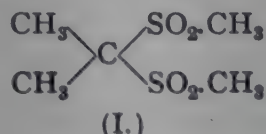
The methods employed in their manufacture are analogous to those employed for sulphonal.

**Trional** forms colourless crystals, M.P.  $76^\circ$ , readily soluble in alcohol and ether, slightly so in water. The dose for insomnia is from 1-2 g., as an anhydrotic from 0.25-0.5 g. It is contra-indicated in certain affections of the heart.



**Tetronal** forms lustrous leaflets melting at  $85^{\circ}$  and possessing the solubilities and general action of the last two drugs. Dose, the same as for trional.

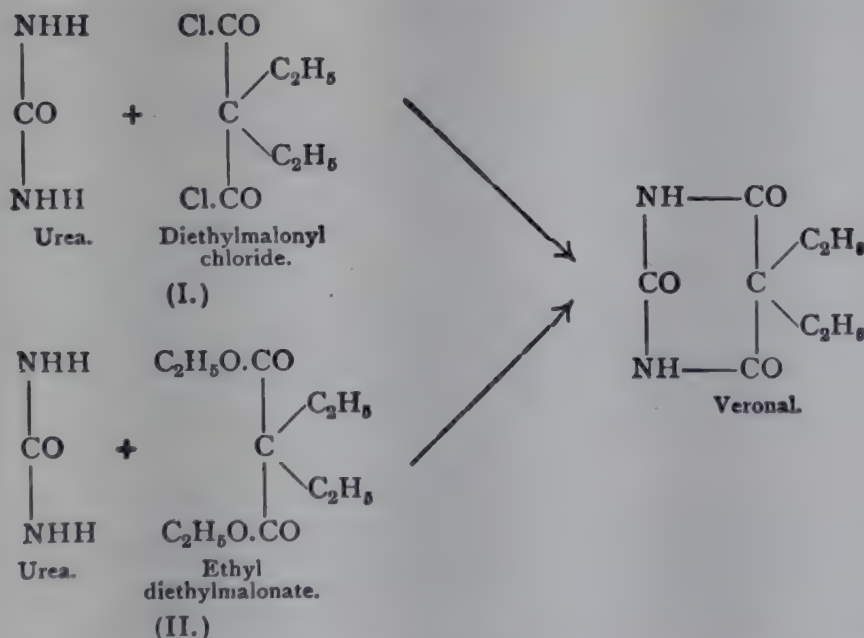
The physiological action of these drugs depends on the presence of the ethyl groups, since dimethylsulphonedimethylmethane (I.) is practically without hypnotic effect. Moreover, the intensity of the physiological action increases as we pass from sulphonal to tetronal, *i.e.*, as the number of ethyl groups increases. In this connection it is interesting to note that if one of the methyl groups in sulphonal be replaced by a phenyl group, the resulting substance (II.) is devoid of soporific effect, but if both methyl groups are so replaced an intensely poisonous compound (III.) is obtained.



Keane,\* in a lecture delivered before the Liverpool Section of the Society of Chemical Industry, draws attention to the fact that the ethyl groups of the sulphone hypnotics are the agents whereby the grouping  $\begin{array}{c} \text{SO}_2- \\ \diagup \quad \diagdown \\ \text{C} \\ \diagup \quad \diagdown \\ \text{SO}_2- \end{array}$ , which is really the carrier of the soporific action, can be brought into combination with the protoplasm of the living organism.

**Hedonal**, methylpropylcarbinolurethane,  $\text{NH}_2 \cdot \text{CO} \cdot \text{O} \cdot \text{CH}(\text{CH}_3)(\text{C}_3\text{H}_7)$ , is prepared by acting on secondary amyl alcohol,  $(\text{CH}_3)(\text{C}_3\text{H}_7) \cdot \text{CHOH}$ , with ethyl chlorocarbonate, and then treating with  $\text{NH}_3$ . Crystals; M.P.  $76^{\circ}$ ; sparingly soluble in cold, easily in hot  $\text{H}_2\text{O}$ . Hypnotic in cases of hysteria or neurasthenia. Dose, 1.5-2 g. in alcohol.

**Veronal**,† diethylmalonylurea, or diethylbarbituric acid,  $\text{C}_8\text{H}_{12}\text{O}_3\text{N}_2$ , introduced into therapeutics in 1903 by Emil Fischer and von Mering, is prepared by the condensation of diethylmalonyl chloride (I.) or ethyl diethylmalonate (II.) and urea:—



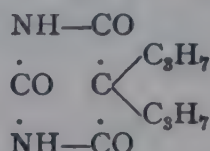
Small transparent crystals; M.P.  $191^{\circ}$ ; soluble in 145 parts  $\text{H}_2\text{O}$  at  $20^{\circ} \text{C.}$ , 12 parts  $\text{H}_2\text{O}$  at  $100^{\circ} \text{C.}$  The monosodium derivative is more soluble, and so is frequently employed. An excellent soporific (dose, 0.5-1 g.). Used in sea sickness, vomiting, etc.

\* *Journ. Soc. Chem. Ind.*, 15th April 1910.

† See Merck's "Annual Reports," 1903-1910, and a pamphlet entitled "Veronal," also published by the same firm.

It is very much to be preferred to other drugs in cases where the patient may have to receive a hypnotic for a protracted period, since there seems to be no evidence to show that it produces a habit, although in time the effective dose of the drug may have to be raised slightly. In such cases the treatment may advantageously be varied by the prescription of proponal (see below). It has been successfully used as a partial substitute for morphine in the early stages of treatment of patients striving to break off a habit for that drug.

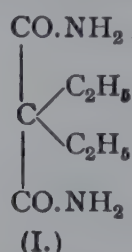
**Proponal\*** is dipropylmalonylurea or dipropylbarbituric acid:—



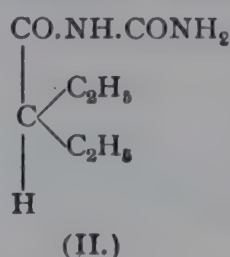
The preparation is analogous to that of veronal. It is less soluble than the latter drug, dissolving in 70 parts boiling and 1,640 parts cold water. Dose in simple insomnia = 0.15–0.2 g.

It not infrequently produces a remarkably prolonged effect, a feeling of drowsiness persisting for some hours after awakening. This drug seems to be quite equal to veronal in its freedom from unpleasant effects.

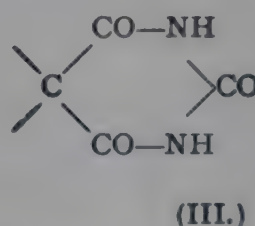
It is probably the presence of the urea residue which is responsible for the soporific effect in veronal and proponal. This is evident from the fact that while the amide of diethylmalonic acid (I.) has no hypnotic effect, diethylacetyl urea (II.)—in which a urea residue has been introduced—is as strong a hypnotic as sulphonal. The action of the urea radical is greatest when it is present in the form of a cyclic ureide, as in the veronal group of hypnotics (III.).



Amide of diethylmalonic acid.  
No hypnotic properties.



Diethylacetyl urea.  
Hypnotic properties.



Hypnotic group in veronal and proponal.  
Strong hypnotic properties.

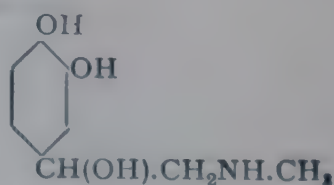
Overton† has shown for a large number of hypnotics that the intensity of the narcotic action of a given drug is proportional to the ratio between its solubilities in oil and in water (*i.e.*, distribution coefficient).

The discovery is important because the material of nerve cells is largely composed of oily or fatty substances (lipoids).

The narcotic drug, after introduction into the system, rapidly finds its way into the blood, in which condition it is practically in aqueous solution; the extent of its narcotic action, or, in other words, the extent to which it permeates the nerve cells, depends, therefore, on the ratio between its solubility in the serum and in the cell lipoids. This applies, of course, to drugs such as chloroform and ether as well as to sulphonal, trional, etc.

## ADRENALINE

**Adrenaline** (epinephrine, suprarenine, hemisine), the active principle of the suprarenal capsules, has the constitution—



Adrenaline forms white, light crystals, M.P. 210°–212°, very sparingly soluble in water, alcohol, and ether; soluble in dilute acids. The aqueous solution has a

\* Merck's "Reports," 1905–1909.

† "Studien über Narcose," Dissertation, Jena, 1901; see also Pflüger's *Archives*, 92, 115–280.



bitter taste and is faintly alkaline. In alkaline and neutral solution it is a strong reducing agent, absorbing oxygen from the air and turning brown, the change being accompanied by a diminution in physiological activity.

Adrenaline is known in all three possible forms, viz., laevo-rotatory (*l*), dextro-rotatory (*d*), and racemic (*dl*).

In the suprarenal capsules only the laevo-rotatory base occurs, and this is by far the most physiologically active, being (as regards rise of blood pressure) twelve to fifteen times stronger than the *d*-modification, and *twice* as strong as the *dl* or racemic variety.

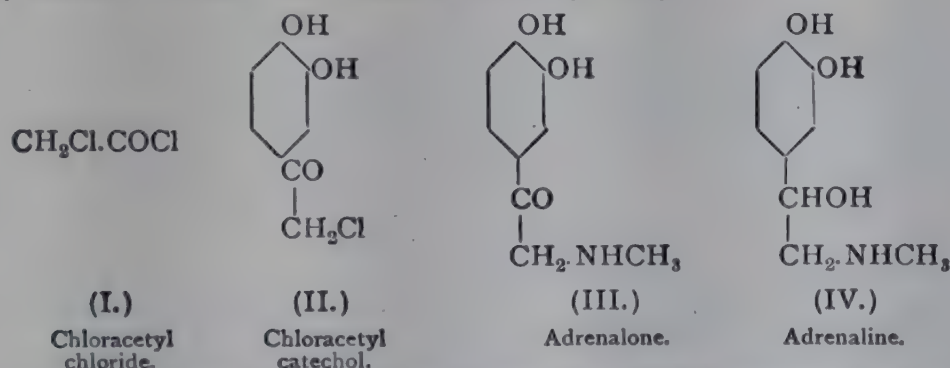
(a) **Extraction of *l*-Adrenaline from the Suprarenal Glands.**—Takamine extracted at 95° C. the disintegrated suprarenal glands of sheep or oxen with water acidulated with HCl or acetic acid, concentrated the extract, added alcohol until no further precipitate was thrown down, filtered, evaporated *in vacuo*, and rendered alkaline with ammonia. In a few hours adrenaline crystallised out and was purified by solution in acid and reprecipitation with ammonia. 112 kg. of fresh tissue yield 125 g. adrenaline.  $[\alpha]_D = -51.4^\circ$  in HCl.

(b) **Synthetic Preparation of Adrenaline (Stolz).**—Chloroacetylchloride (I.) or a mixture of monochloroacetic acid and phosphorus oxychloride is made to react with catechol whereby chloroacetylcatechol\* (II.) is produced. This is then mixed with alcohol, and an aqueous solution of methylamine run into the cooled mixture.

The methylamine salt of the chloroacetylcatechol is first produced, but on standing changes to methylaminoacetylcatechol (III.) which crystallises out. This ketone is known as adrenalone; its salts with acids differ from those of adrenaline in that sodium acetate precipitates from them the free base.

By reduction of a solution of adrenalone sulphate by means of aluminium turnings† in presence of mercuric sulphate, adrenaline (IV.) is obtained.

Dakin‡ has also reduced adrenalone electrolytically.



This preparation of synthetic adrenaline was carried out by Stolz whilst working in the laboratories of Messrs Meister, Lucius, & Brünig.

The product is known as **synthetic or racemic** adrenaline, and is about half as physiologically active as the natural *l*-rotatory adrenaline. The resolution of this racemic adrenaline into *l*-adrenaline—identical in all respects with the natural product—and *d*-adrenaline, has been achieved by Flächer (also of Meister, Lucius, & Brünig's staff) as follows:—

**Resolution of Synthetic Racemic Adrenaline.**§—Synthetic adrenaline is dissolved in a hot methyl alcohol solution of the molecular equivalent of *d*-tartaric acid, the alcohol removed *in vacuo* at 35°-40°, and the residue crystallised by seeding with the acid *d*-tartrate of *l*-adrenalin. The crystals of the acid *d*-tartrate of *dl*-adrenaline are then stirred with methyl alcohol, when the acid *d*-tartrate of the *l*-base remains undissolved while the isomeric salt passes into solution. The crystals are filtered off, washed, and recrystallised from alcohol until a product is obtained melting at 149°. The **laevo-adrenaline** recovered from this showed a rotation of  $[\alpha]_D -51.4^\circ$  in dilute hydrochloric acid solution, melted at 211°-212° (the melting point of *dl*-adrenaline), and was identical in all respects with the natural *l*-adrenaline obtained from the suprarenal glands.

The **dextro-adrenaline** is obtained by regenerating the base from the methyl alcohol mother liquors, and submitting it to a similar treatment with *l*-tartaric acid, M.P. 211°-212°;  $[\alpha]_D = +51.9^\circ$  in dil. HCl. Very little physiological action.

\* *Bull. Soc. Chim.* [3], 12, 1911 (1894).

† *Cent. Blatt.*, 1905 (I.), 315.

‡ *Ibid.* (II.), 57.

§ Flächer, *Hoppe-Seyler's Zeitschrift*, Vol. 58, part 3, p. 189.



**Clinical Uses of *l*-Adrenaline.**—When injected subcutaneously it intensely contracts the arteries and increases the blood pressure.

So enormously powerful physiologically is adrenaline that the injection of one-millionth of a gram for every 2 lbs. weight of an animal causes the blood pressure to suspend a column of water 7 in. higher than it would otherwise do. A dose of one-twentieth of a milligram intravenously injected in rabbits doubles the general arterial blood pressure, and less than one-millionth of a gram gives a distinct action.

The contractile effect on the arteries is so great that it drives blood away from the injected tissues and thus allows "bloodless" surgery, adrenaline being to-day the most valued styptic known.

It has been used in ophthalmic surgery in conjunction with cocaine or similar drugs (see Section I., p. 603) for the production of local anæsthesia along with anæmia of the conjunctiva. If administered along with an anæsthetic such as chloroform or ether, adrenaline tends to prevent the fatal collapse which sometimes occurs under these conditions, while for minor operations, as in dentistry, when employed along with cocaine, it prevents severe bleeding.

It is employed in the earlier stages of Addison's disease, which arises from a diseased condition of the suprarenal glands. It is also used in cases of catarrh. Strength of solution used for injection is 0.1-0.01 per cent., maximum dose for injection = 0.0005 g.

The introduction of adrenaline into Surgery is largely due to the scientific work of the firm Meister, Lucius, & Brünig.

A number of important recent researches have been made on the connection between the physiological action of adrenaline and its chemical constitution, with the object of ultimately synthesising other drugs with similar or more powerful characteristics. See Dakin, *Proc. Roy. Soc. Lond.*, 76, Series B, 498-503; also *Cent. Bl.*, 1905, ii. 1458, and *Journ. Physiol.*, 1905, 32, p. 35; Loewi and Hans Meyer, *Cent. Blatt.*, 1905, 1111; Barger and Dale, *Journ. Physiol.*, 1910, 41, 19.



is closely allied to adrenaline both in formula and physiological action. It is prepared by the degradation of papaverine (compare Pyman, *Trans. Chem. Soc.*, 1910, 97, 264), and is placed on the market by Burroughs Wellcome & Co. under the name "**Epinine.**"

### ERGOT, ETC.

**Ergot** (*Claviceps purpurea*, *Sclerotium clavus*, and *Spermaldia clavus*), a dark-coloured fungus which attacks damp rye and other grasses, and when contained in flour causes the disease known as **Ergotism**, is much used in midwifery for causing powerful contractile action of the pregnant uterus. When injected, it produces a rise in blood pressure, and is sometimes used to check hæmorrhage from the lungs and other internal organs.

Formerly no method of testing the efficiency of the various ergot preparations was known, but now the strength is ascertained by noting the quantity required to blacken (cause gangrene) a cock's comb.

Ergot is detected in flour by extracting with boiling alcohol, acidifying with  $\text{H}_2\text{SO}_4$ , and examining the alcoholic extract spectroscopically. If ergot is present the solution is reddish and shows characteristic absorption bands.

**Chemical Constituents of Ergot.**—Ergot is a complex mixture of alkaloids. The chief physiologically active ones isolated are:—

\* **Ergotoxine**,  $\text{C}_{35}\text{H}_{41}\text{O}_6\text{N}_5$ , white amorphous powder, is the physiologically active principle of ergot, since it produces a strong rise in blood pressure, causes gangrene of the cock's comb, and powerfully contracts the pregnant uterus, although having little effect on the isolated non-pregnant uterus.

***p*-Hydroxyphenylethylamine**,  $\text{HO} \begin{array}{c} \diagup \quad \diagdown \\ \text{C}_6\text{H}_4 \\ \diagdown \quad \diagup \end{array} \text{CH}_2 \cdot \text{CH}_2 \cdot \text{NH}_2$ , is present in the aqueous extract of ergot, from which it was extracted and later on synthesised by

\* Barger and Carr, *Trans.*, 1907, 91, 347; Barger and Ewins, *ibid.*, 1910, 97, 284.



Barger (*Proc. Physiol. Soc.*, 1909, 37, 77; *Biochem. Journ.*, 1907, ii. 240; *Trans. Chem. Soc.*, 1909, 95, 1123, 1720). M.P. 161°. Is now placed on the market by Messrs Burroughs Wellcome & Co. under the name **Tyramine**. In addition to raising the blood pressure and producing strong contraction of the pregnant uterus, it greatly increases the vigour of the heart's action, and may be administered in case of shock or collapse.

**Iso-amylamine**,  $(\text{CH}_3)_2\text{CH}.\text{CH}_2.\text{CH}_2.\text{NH}_2$ , isolated by Barger (*loc. cit.*) from aqueous extract of ergot by steam distillation. Increases the blood pressure and contracts pregnant uterus.

Both *p*-hydroxyphenylethylamine and isoamylamine are present in putrid meat.

**4 (or 5)- $\beta$ -Aminoethylglyoxaline**, also known as  $\beta$ -iminazolylethylamine, is also contained in ergot. (Barger and Dale, *Trans.*, 1910, 97, 2592; Ewins and Pyman, *Trans.*, 1911, 99, 339; Ackermann, *Zeitsch. Physiol. Chem.*, 65, 1910, 504). It

has the constitution

$$\begin{array}{c} \text{CH}-\text{NH} \\ \parallel \quad \diagdown \\ \text{NH}_2.\text{CH}_2.\text{CH}_2.\text{C}-\text{N} \\ \parallel \quad \diagup \\ \text{CH} \end{array}$$

and is prepared synthetically

(Windaus and Vogt, *Ber.*, 40, 1907, 3691; Pyman, *Trans.*, 1911, 99, 668). It is now placed on the market by Burroughs Wellcome & Co. under the name "**Ergamine**." It decreases the blood pressure and powerfully contracts the isolated uterus even in a non-pregnant condition.

**Hordenine**,  $\text{HO}.\text{C}_6\text{H}_4.\text{CH}_2.\text{CH}_2.\text{N}(\text{CH}_3)_2$ , was isolated by Leger\* from barley-malt germs, in which it is present to 0.2-0.5 per cent., by extracting with alcohol in the presence of tartaric acid, filtering, neutralising, extracting with ether, and crystallising the product from alcohol. It is a strong base, sparingly soluble in water, soluble in alcohol, ether,  $\text{CHCl}_3$ , etc., and forms crystalline salts with acids. Hordenine retards coagulation of the blood and when injected raises the blood pressure, although not to the same extent as adrenaline or the ergot bases. Not very toxic. Used in dysentery and as a heart tonic. Preparations are placed on the market by Merck and by Burroughs Wellcome & Co. It has been synthesised by Barger (*Trans. Chem. Soc.*, 1909, 95, 2193).

## SYNTHETIC DRUGS USED IN PARASITIC DISEASES, SUCH AS SLEEPING SICKNESS, SYPHILIS, ETC.

**Atoxyl, Arsamin, or Soamin**, the mono-sodium salt of *p*-aminophenylarsonic acid,  $\text{NH}_2.\text{C}_6\text{H}_4.\text{As} \begin{array}{l} \nearrow \text{O} \\ \searrow \text{OH} \\ \searrow \text{ONa} \end{array}$ , is prepared by heating arsenic acid with aniline at 190°-200° C., converting into the sodium salt by agitating with  $\text{Na}_2\text{CO}_3$ , and recrystallising from water.

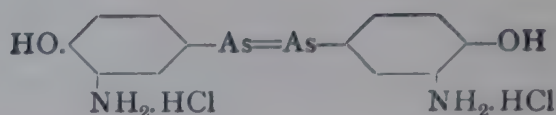
A white powder, tasteless and odourless, easily soluble in  $\text{H}_2\text{O}$ . Decomposes in stomach and so is given subcutaneously. Used in the treatment of sleeping sickness and syphilis. Dose, about 0.5 g. Incautious treatment may lead to blindness and symptoms of poisoning, (headache, colic). Also used in tuberculosis.

**Acetylatoxyl or Arsacetin**,  $\text{CH}_3\text{CO}.\text{NH}.\text{C}_6\text{H}_4.\text{As} \begin{array}{l} \nearrow \text{O} \\ \searrow \text{OH} \\ \searrow \text{ONa} \end{array}$ , is soluble in water (1 part in 10). More chemically stable and less toxic than atoxyl. It has been successfully employed in sleeping sickness, skin diseases, and syphilis. Dose, 0.6 g. injected in 10-15 per cent. solution.

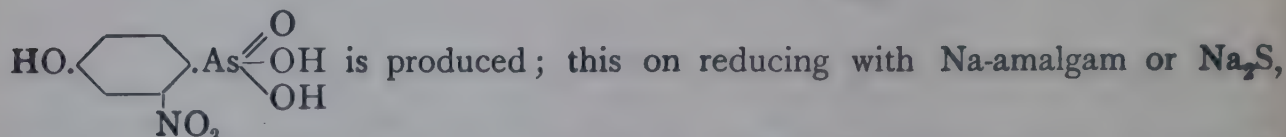
\* *Compt. rend.*, 1906, 142, 108, 143, 234, 916 et seq.



**Salvarsan**, "606," is dihydroxydiaminoarsenobenzene dihydrochloride, and has the constitution:



It is prepared, according to the English Patent 13,485, 1910, by nitrating the Na-salt of *p*-hydroxyphenylarsonic acid,  $\text{HO} \cdot \text{C}_6\text{H}_4 \cdot \text{As} \begin{smallmatrix} \text{O} \\ \text{OH} \end{smallmatrix}$ , whereby the nitro-body



condenses, with the ultimate production of the dihydroxydiamino-compound, whose hydrochloride is known as **Salvarsan**. Salvarsan is a bright yellow powder supplied in glass tubes filled with an inert gas to prevent oxidation.

The introduction of **Salvarsan** by Ehrlich and Hata in 1910-1911 caused a sensation in the medical world. It is stated to be a specific cure for syphilis, a single injection into the buttocks having effected a complete cure in many cases. It is placed on the market by Meister, Lucius, & Brüning. See "Salvarsan," by Martendale and Westcott (London, 1911); also Ehrlich and Hata's treatise, "Die Experimentelle Chemotherapie," Berlin, 1911.

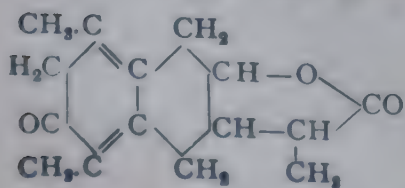
**Arsenophenylglycine** ("418"), a predecessor of salvarsan, has the formula  $\text{COOH} \cdot \text{CH}_2 \cdot \text{NH} \cdot \text{C}_6\text{H}_4 \text{---As=As---} \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{CH}_2 \cdot \text{COOH}$ . Also a powerful curative agent for syphilis, but not so popular as salvarsan.

**Ichthyol** is a volatile oil containing sulphur obtained by heating "stink-stone" or "oil-stone"—a bituminous schist found in the Tyrol (Seefeld). The salts of ichthyol sulphonic acid (obtained by treating ichthyol with concentrated  $\text{H}_2\text{SO}_4$ ) are used therapeutically, the ammonium salt, **ammonium "sulphoichthyolicum,"** being obtained by neutralising the sulphonic acid with ammonia and evaporating to a syrup. It is sometimes called "ichthyol." It forms a reddish brown syrup, soluble in water, with a smoky taste and smell. Much used externally in cases of skin diseases and internally in cases of tuberculosis, catarrh of the lungs, chronic diseases of the stomach and intestines. The Na-, Li-, and Zn salts are also used.

**Ichthyol-Albumen** (=Ichthalbine) is obtained by precipitating albumen solution with a solution of ichthyol sulphonic acid. Grey-brown powder, soluble in water, insoluble in the stomach. It decomposes in the intestine into ichthyol and albumen, and is used for intestinal catarrh.

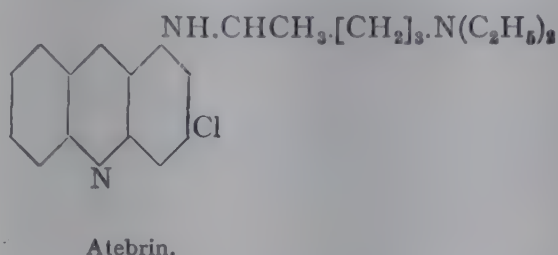
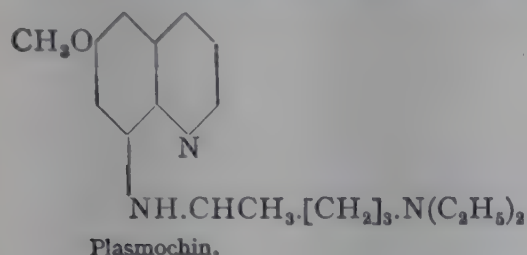
**Ichthoform** is a compound of ichthyol sulphonic acid and formaldehyde. Dark powder, insoluble, almost odourless and tasteless. Used externally as an **iodoform substitute** for wounds, and internally as an intestinal antiseptic.

**Santonine**,  $\text{C}_{15}\text{H}_{18}\text{O}_8$ , the lactone of santoninic acid,  $\text{C}_{15}\text{H}_{20}\text{O}_4$ , is separated from the blossoms of wormseed and used for destroying intestinal worms. Dose, 0.025-0.05 g. twice daily for children. Maximum dose, 0.1-0.3 g. per diem. Colourless, odourless crystals, M.P. 170°. Sparingly soluble in cold water, more soluble in hot, readily soluble in alcohol, ether, chloroform. Turns yellow in light.





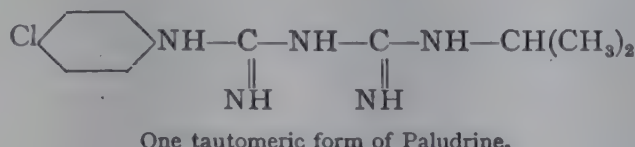
The chemotherapy of malaria has recently reached a place of great importance in synthetic organic chemistry. As Japan had control of the majority of the world's quinine, the search for a substitute was of special importance during the last war. It probably began with Roehl's work on the transmission of malaria-like infections in small birds by blood injections. Thus **Plasmochin** (pamaquine) and **Atebrin** (mepacrine) were evolved.



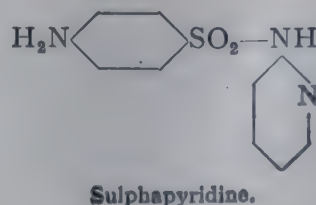
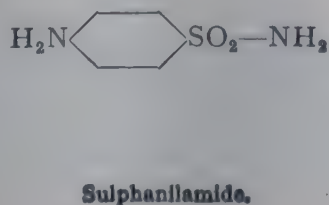
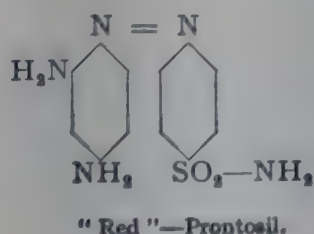
Pamaquine was derived from the quinoline nucleus of the quinine molecule, whereas mepacrine with the same side chains attached to an acridine nucleus has a structural relation to methylene blue.

The new British product **Paludrine** is superior to mepacrine for the treatment of malaria and was the outcome of intensive wartime work by the research department of I.C.I. Pharmaceuticals at Blackley. Among special features of this work are the elaboration of the biological test to enable estimates to be obtained of the prophylactic, suppressive, and truly curative effects of the successive compounds tried in arriving at this optimum; and, on the other hand, the discovery of salient features of chemical structure and behaviour associated with the desired chemotherapeutic properties.

The structure ultimately found to give the optimum activity so far attained is decidedly simpler than that of mepacrine (see formulæ above). In the production of paludrine it has been the aim to produce a material combining high effectiveness against malarial infection, freedom from danger, and production on a large scale at a low cost so that it can be distributed amongst the populations of malaria-infected countries for habitual consumption.

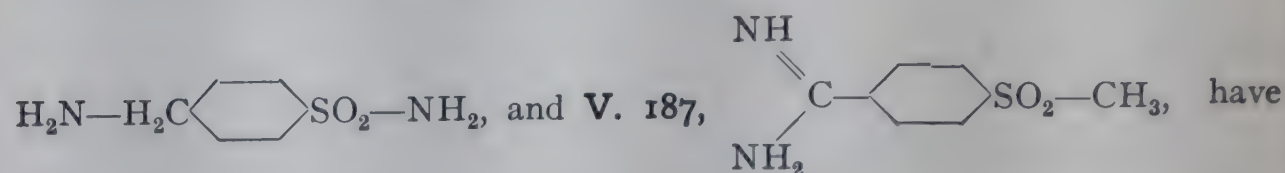


**The Sulpha-drugs.**—In 1935 Domagk discovered that the red dye **Prontosil** was an effective chemotherapeutic agent for the experimental streptococcal infections in mice. This dye was found to have no action on artificial streptococcal cultures. Following this discovery it was found that the essential therapeutic agent in prontosil was the sulphanilamide group. It was then found that sulphanilamide in any concentration tolerable by a living being was not effective in destroying streptococci but inhibited their multiplication so that the natural powers of recovery of the patient could take effect. Many more sulphanilamide derivatives such as sulphadiazine, sulphaguanidine, sulphamethazine, sulphapyridine, and sulphathiazole were then investigated. The formulæ of three of the materials mentioned above are:



These and related materials have revolutionised the treatment of diseases such as pneumonia, cerebrospinal fever, and bacillary dysentery.

It has been found that the bacteriostatic action of the sulphanilamides are due to the fact that they occupy the place normally taken by *p*-aminobenzoic acid in the growth metabolism of the bacteria. Two other antibacterial agents—**Marfanil**,



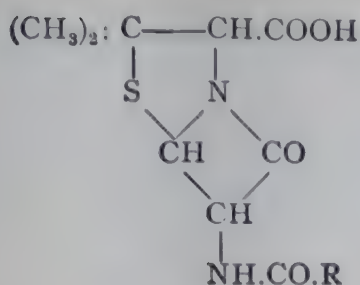
proved very effective in suppressing bacterial wound infections, but the action of neither of these is affected by the presence of *p*-aminobenzoic acid. It is thought that the growth metabolism of bacteria requires other materials besides *p*-aminobenzoic acid and that these are replaced by marfanil in a similar way to that of *p*-aminobenzoic acid by, say, sulphapyridine.

**Penicillin.**—The isolation of penicillin is one of the landmarks of British medical organic chemistry. Fleming, in 1929, and Clutterbuck, Lovell and Raistrick, in 1932, drew attention to the instability of penicillin. It was probably due to the difficulty encountered in the isolation of this material that eleven years elapsed between the pioneer work and the discovery of the unique chemotherapeutic properties of penicillin. This work took place at Oxford in 1940, and was carried out by Chain, Flory, Gardner, Heatley, Jennings, Orr-Ewing, and Sanders. It was shown that penicillin was an acid of low molecular weight which could be extracted from the acidified culture medium but which lost its antibacterial activity on evaporation of the ether. On keeping the solution neutral it was found that the antibacterial activity could be retained and the penicillin salt transferred to an aqueous solution. On evaporating this to dryness from the frozen state the resultant brown powders were found to possess remarkable powers of protecting mice from infection with streptococci, staphylococci, and vibrio septique which would otherwise prove fatal. When purer preparations were tried on man it was recognised that penicillin was to be a powerful tool in the fight against several of the more dangerous of human ailments. The elucidation of the structure became a matter of extreme importance.

The small amount of material available rendered the task of analysis more difficult than it need have been, but crystallographic examination offset this disadvantage somewhat. By 1943 all the major chemical concerns, both in this country and in America, were working at high pressure towards increasing the supply and elucidating the structure of penicillin. By 1944 full exchange of information between America and Britain was taking place. A compendium of 700 monographs, written by British and American workers, has been published by the Princeton University Press.

**The Chemical and Physical Properties of the Penicillins.**—It was found early in the work that there existed a number of penicillins differing in chemical composition but possessing similar chemical and biological properties. It was shown that the penicillins possessed a common nucleus as follows:





R may be a benzyl, heptyl, pentenyl, amyl, or other group. The penicillins are strong, monobasic acids with a pH of about 2.9. The penicillins are stable in their ether, chloroform, and ester solutions below 7° C. In aqueous solution the penicillins are only stable in the form of their salts, *i.e.*, at a pH of 5–8. In acid or alkaline solution they rapidly lose their biological activity. The alkali salts of penicillin may be crystallised readily. The sodium salt of benzylpenicillin was first crystallised by MacPhillamy and Wintersteiner in July 1943. No other metal salts of benzylpenicillin apart from the alkali metal salts have been crystallised, but several crystalline salts with organic bases are known, *e.g.*, the benzylpenicillin salt of triethylamine.

The penicillins lose their biological activity in the presence of other reagents besides acids and alkalis. They are inactivated by zinc, cadmium, lead, mercury, and copper in a catalytic fashion. They are also inactivated by primary alcohols and amines. There is an enzyme, “penicillinase,” which also decomposes penicillin.

When penicillin has been prescribed by the medical profession it is important that it be used within a certain time. This is because penicillin is still to be regarded as an unstable material and, although its stability has been improved recently, seldom remains active for more than twelve months at ambient temperatures.

Attempts are being made to synthesise penicillin and have been successful in that a substance which behaves biologically and chemically in an identical way to penicillin has been obtained, but to date the yields are so low that it is not likely that synthetic methods will replace the fermentation method used at present.

In the latter a mould by the name of *Penicillium notatum* is grown in a nutrient culture medium in which the temperature, pH, and composition is carefully controlled. The presence of various other materials accelerate the growth and increase the yield. The culture medium may be a broth, but this has been replaced by a glucose solution containing mineral salts such as sodium nitrate, potassium dihydrogen phosphate, potassium chloride, magnesium sulphate, and ferrous sulphate. The concentration of penicillin is a delicate and laborious process. The principle of the process depends on the fact that penicillin is soluble in organic solvents such as ether and amyl acetate, whereas the sodium and potassium salts of penicillin are soluble in water. By means of the two different types of solvent the impurities are separated out.

Penicillin appears to be one of the most versatile of chemotherapeutic materials. It is most efficient in its bacteriostatic effect on staphylococci, but is also used for sore throats, pneumonia, diphtheria, gas gangrene, and meningitis. Open wounds are often treated with penicillin.

**Streptomycin.**—In this brief survey of modern synthetic drugs it has not been possible to include streptomycin, the action of which is not fully known. For a study of this drug the reader is referred to a recent publication by the Glaxo Laboratories.



## VEGETABLE ALKALOIDS

**Alkaloids of Opium.**—Opium is a very complex mixture containing along with protein matter and various acids, carbohydrates, gums, waxes, etc., numerous alkaloids of which the most important are: Morphine, about 9 per cent., Narcotine 5 per cent., Papaverine, 0.8 per cent., Thebaine, 0.4 per cent., Codeine, 0.3 per cent., Narceine, 0.2 per cent.

**Morphine**,  $C_{17}H_{19}NO_3$ , the most important, is extracted as follows: The aqueous extract of opium is concentrated, and alkaloids precipitated with sodium carbonate. The precipitate is extracted first with water, and then with cold alcohol when most of the morphine remains behind. This is dried, dissolved in dilute acetic acid (any narcotine is insoluble), filtered through animal charcoal and precipitated with ammonia. Purified through its salts or by crystallising from boiling alcohol. Dose of morphine hydrochloride,  $\frac{1}{8}$ – $\frac{1}{2}$  grain.

**Atropine**,  $C_{17}H_{23}NO_3$ , occurs in the deadly nightshade (*Atropa belladonna*) and in *Datura stramonium*. It forms heavy needles of M.P.  $115^\circ$ , and is intensely poisonous, and strongly dilates the pupil of the eye, for which purpose a 0.5 per cent. solution is used in ophthalmology. Maximum dose = .001 g.; maximum per day, 0.003 g.

It is also used as a narcotic, and in the night sweats of phthisis. Its constitution is given under **Cocaine** (section on **Local Anæsthetics**).

**Strychnine**,  $C_{21}H_{22}N_2O_2$ , occurs along with brucine,  $C_{23}H_{26}N_2O_4$ , in the seeds of *Strychnos nux vomica*.

**Extraction.**—The crushed, water-sodden nuts are ground to a pulp, and extracted with hot alcohol, the latter evaporated, the extract treated with lead acetate, and excess of lead removed by  $H_2S$  or  $H_2SO_4$ . The strychnine is then precipitated with caustic soda, the more soluble brucine remaining almost completely behind.

Colourless crystals, intensely poisonous, a typical spinal poison. Dose,  $\frac{1}{30}$ – $\frac{1}{12}$  of a grain. It is a valuable tonic, and is employed in paralysis, and in cases of lead poisoning.

**Quinine**,  $C_{20}H_{24}N_2O_2$ , is obtained from various kinds of cinchona bark, in which it occurs along with other alkaloids such as quinidine, cinchonine cinchonidine, etc.

**Extraction.**—The powdered bark is mixed with lime and extracted with high boiling petroleum, the solution being then shaken with dilute sulphuric acid and neutralised while hot with  $Na_2CO_3$ . The most of the quinine then separates as sulphate, which is further purified by precipitating as insoluble tartrate with Rochelle salt solution.

A white crystalline powder almost insoluble in water, sparingly soluble in cold alcohol, the aqueous solution of its sulphate fluoresces blue. Perhaps the most important drug known, its annual production amounting to 485,900 kg. Synthetic antimalarials are more often used nowadays.

**Pilocarpine**,  $C_{11}H_{16}N_2O_2$ , occurring in Jaborandi leaves, is the physiological antithesis of atropine. It is a thick liquid and is used as a sudorific and to check salivation.

For the chemistry of pilocarpine see papers by Jowett, *Trans.*, 1901-1905.

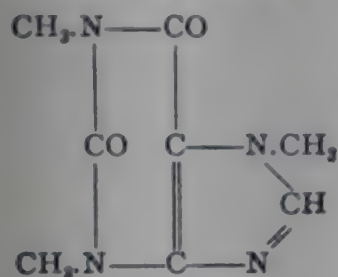
**Hydrastine**,  $C_{21}H_{21}NO_6$ , found in the root of a North American plant *Hydrastis canadensis*, is employed similarly to ergot.

**Veratrine.**—The commercial product, obtained from the seeds of *Veratrum sabadilla*, is a mixture of various alkaloids. It is a white powder causing violent sneezing and general irritation of the mucous membrane when inhaled.

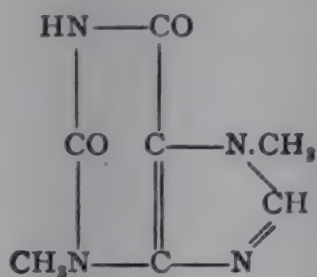


**Yohimbine** is an alkaloid obtained from the Yumbehoa tree (Africa). It is employed internally in cases of impotence.

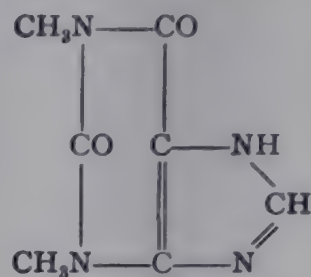
**Purine Alkaloids.**—Three important drugs belonging to the purine compounds are Caffeine,  $C_8H_{10}O_2N_4 + H_2O$ , Theobromine,  $C_7H_8O_2N_4$ , and Theophylline or Theocine,  $C_7H_8O_2N_4$ .



Caffeine.  
1:3:7-Trimethylxanthine.



Theobromine.  
3:7-Dimethylxanthine.



Theophylline.  
1:3-Dimethylxanthine.

**Caffeine** occurs in tea and coffee, about 1.4 per cent. in tea. From the waste dust of tea it is extracted by boiling with water, precipitating tannin with lead acetate, removing excess of the latter with  $H_2S$ , filtering, and concentrating, when caffeine crystallises out. It is also obtained as a byproduct in the manufacture of caffeine-free coffee. Unroasted coffee beans are treated with superheated steam and extracted with benzene, whereby much of their caffeine is removed. It is now prepared on the large scale from guano by Böhringen & Sons, of Mannheim.

Caffeine forms white silky needles which lose water at  $100^\circ$ , sublime at  $180^\circ$ , and melt at  $230.5^\circ$ . It is soluble in 80 parts of water at  $15^\circ$  and in 2 parts of boiling water, but is sparingly soluble in many organic solvents such as cold alcohol. Chloroform readily dissolves it.

Used in headache and neuralgia alone or combined with phenacetin, and as a heart tonic. Dose, 0.5 g.; maximum daily dose, 1.5 g. It is employed internally and subcutaneously.

**Theobromine**, a colourless, odourless, crystalline powder, sublimes at  $290^\circ$ , neither melting nor decomposing. It occurs in cocoa. Combined with a molecular proportion of sodium salicylate, its sodium salt is employed under the name of Diuretin. This is a white powder, soluble in water, and employed in dropsy and in diseases of the kidneys and heart. Theobromine has been synthesised by Traube (*Berichte d. deutschen Chemischen Gesellschaft*, 33, 1371 and 3035) starting from cyanoacetic acid and methylurea.

**Theophylline** or Theocine is a stronger diuretic than theobromine. It occurs to a small extent in tea leaves. Sodium theophylline acetate is a valuable diuretic.

**Synthetic Preparation.**—See D.R. Pat., 151,133, 144,761, 148,208, 138,444. Theophylline itself forms colourless crystals, M.P.  $208^\circ$ . It is difficultly soluble in water, hence the use of soluble double compounds.

The writer desires to thank the following firms for much information regarding some of the synthetic drugs:—Messrs Burroughs Wellcome & Co., London; Messrs Meister, Lucius, & Brünig, Höchst; Messrs Merck, Darmstadt; Messrs Evans, Sons, Lescher, & Webb, Liverpool.





SECTION XXII

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The Plastics Industry





# THE PLASTICS INDUSTRY

By E. I. COOKE, M.A.(Cantab), B.Sc., A.R.I.C.

## I. INTRODUCTION

THE original article, of which the following forms only a part, had to be reduced considerably for reasons beyond the writer's control. The following items have been completely removed, but literature to which the reader may refer is given in their place.

Expanded plastics.

Surface dyeing of plastics.

Terylene.

Ethyl cellulose, benzyl cellulose.

High-frequency heating.

Casein and protein plastics.

Critical comparison of properties of plastics and the uses to which many have been placed.

Many illustrations. Similar ones may be seen in the literature.

## LITERATURE

REDDISH.—*Trans. Far. Soc.*, 46, Part 6, pp. 459-475. June 1950.

HERCULES POWDER CO.—"Ethyl Cellulose and its Properties."

SIMMONDS, ELLIS AND BIGELOW.—"Handbook of Plastics."

"Thorp's Dictionary of Applied Chemistry."

D. TRIALL.—"Ethyl Cellulose and Benzyl Cellulose."

Monograph issued by the Institute of the Plastics Industry.

BROWN.—"Plastics," 1943, 7, 349.

DRING.—"Plastics," 1944, 8, 10.

BRAJNIOFF.—"Plastics," 1942, 6, 373.

SUTERMEISTER AND BROWNE.—"Casein and its Industrial Applications." Reinhold Corp., N.Y. 1939.

*Industrial and Engineering Chemistry*, 1936, 28, 774; 1940, 31, 31; 1940, 31, 1549; 1940, 32, 906.

It is not easy to find a definition of plastics which will not invoke criticism. Some regard plastics as necessarily synthetic materials, while others divide plastics into natural and synthetic plastics. The main objection to this subdivision is that the definition of a natural plastic becomes nearly impossible—any naturally occurring material which softens on heating is then classed as a natural plastic.

In this section we define a plastic as a synthetic polymeric organic material which is plastic at some stage of its existence. If the latter material softens on heating and remains soft up to its decomposition point, we define it as a thermoplastic; but if the material softens on heating and then gradually hardens (cures or sets) as the temperature is further raised, we define the material as a thermo-setting or a thermo-hardening plastic.

**Perspex** (polymethylmethacrylate) is an example of a thermoplastic, while **Bakelite** (phenolformaldehyde) is an example of a thermo-setting plastic.

There are a number of natural resins which some regard as plastics but which are dealt with elsewhere in this book. These are bitumen, shellac, cellulosic compositions (regenerated cellulose), and rosin. Gutta-percha—a natural material—is dealt with here as a "natural plastic."

Both thermoplastics and thermo-setting plastics are soft at some stage of their life. It is at this point that the necessary processing and shaping is carried out, *e.g.*, film forming. Both thermoplastics and thermo-setting plastics exhibit the common feature of a complex polymeric structure. In the case of the thermo-setting plastics this complex structure becomes more complex on curing.

The desirable properties of a plastic may be listed as follows:—

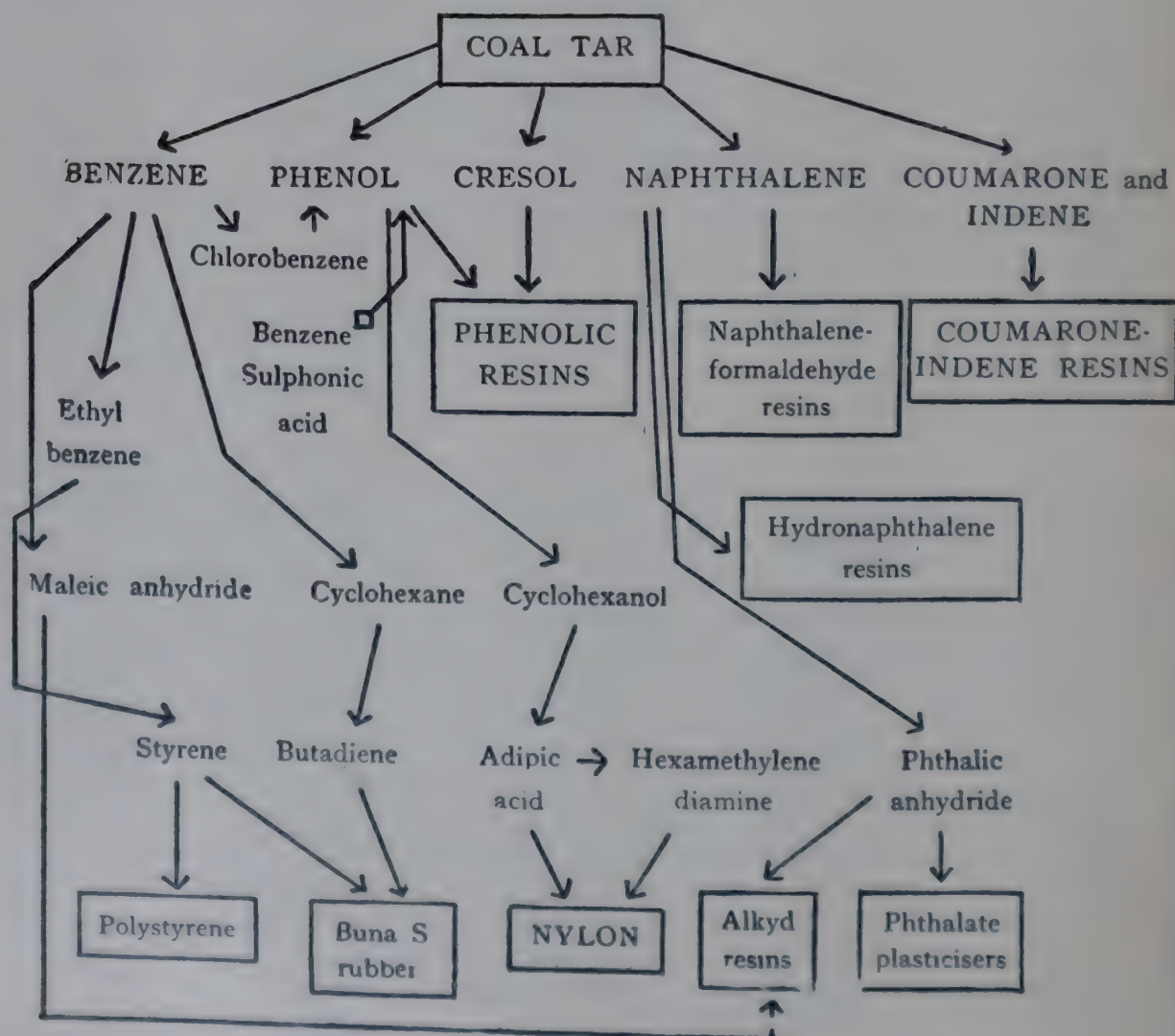
1. High plasticity at the shaping temperature, *i.e.*, easily moulded at the moulding temperature.

2. The material should not have any tendency to deform in the temperature range within which it is to be used. These properties are shown by relatively few thermoplastics to any degree of satisfaction. Three of these are polythene, polyvinyl chloride, and nylon. These three materials have relatively flat plasticity curves up to the softening-point.

**Sources of Plastics.**—The most important materials used in the manufacture of plastics are acetic acid, acetone, acetylene, alcohol, benzole, butyraldehyde, cresols, ethylene dichloride, formaldehyde, phenol, urea, wood pulp, and cotton linters. In addition to these, many high-boiling esters, such as tricresyl phosphate, are used as plasticisers. Details as to how each one of these is used will be given in a later section.

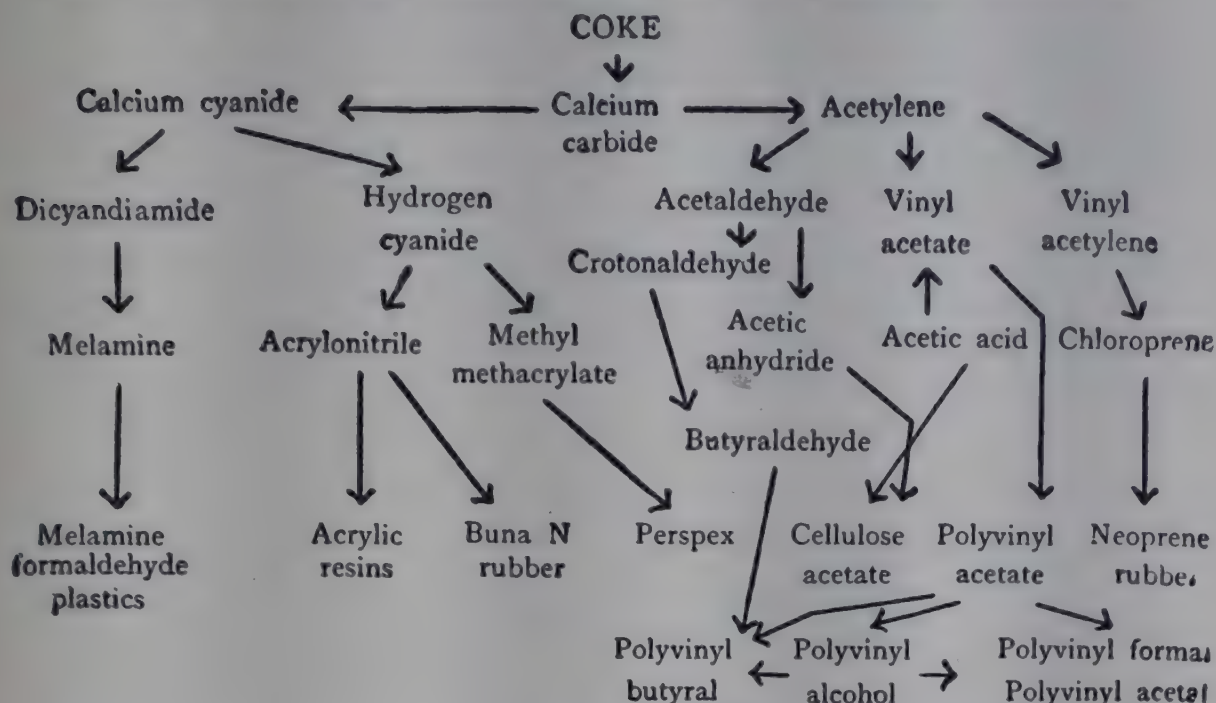
The principal sources of the above raw materials are the coal industry and the agricultural industry, although the petroleum industry is rapidly becoming more important as a source of ethylene, butadiene, and styrene for plastics manufacture (see section on Petroleum).

The following trees give an indication of the plastics obtained from coal tar:—

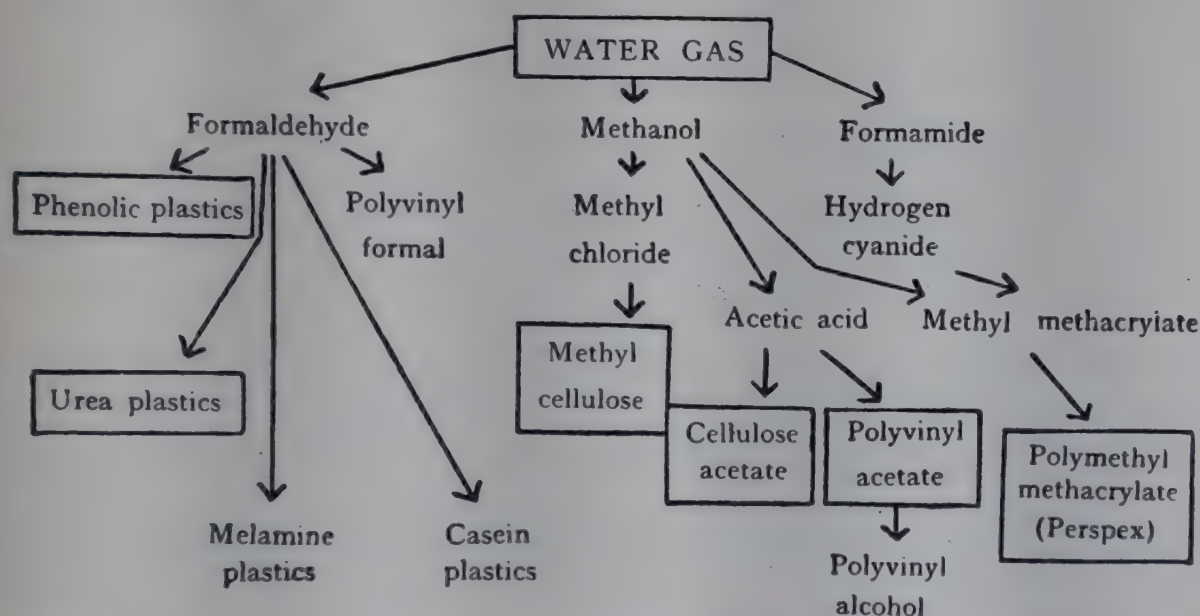




Then from coke we may obtain another range of plastics as follows:—



From water gas we may obtain the following plastics:—



Agriculture contributes to the plastics industry in the following ways. Sawdust is provided for filling phenol-formaldehyde resins (*q.v.*). Cotton linters are also provided for this purpose. The basic material for the manufacture of cellulose acetate, cellulose nitrate, and ethyl cellulose is cellulose from cotton seeds. 175 lb. of cotton are obtained from a ton of cotton seeds.

Corn, sugar, and protein plants such as soya have been used for the manufacture of alcohol and synthetic fibres.

A more intelligent use of agricultural waste is the manufacture of furfural from oat hulls, straw, and corn cobs, of which probably 1,000 million tons are available every year.

**Uses of Plastics.**—There are two possible ways of using present and future plastics. They may either be used to replace familiar materials, for example, the replacement of upholstery by plasticised polyvinylchloride, china crockery by plastic crockery, silk stockings by nylon and rayon stockings—or they may be used far more ingeniously to provide a material which nature has not provided, at least to us living on this planet. Examples of this use are the manufacture of

polythene to provide a flexible high-frequency dielectric in radar—unheard of before the 1939–45 War—and the manufacture of highly plasticised polyvinyl-chloride dolls which have a flesh-like feel and appearance.

Probably nylon is the most satisfactory of all plastics if all properties are considered. Polythene is probably a good second.

The largest users of plastics are the electrical industry. Manufacturers of domestic ware, the building industry, and the clothing industry come next in order.

The equipment required for the plastics industry is heavy and costly. For example, mills, mixers, extruders, and presses are essential, and together with the large number of processes required are the cause of the rather high price of most plastics.

## II. THE INDUSTRIAL MANUFACTURE OF SOME OF THE COMMONER PLASTICS

### GUTTA-PERCHA

By D. W. IZOD, A.I.R.I.

#### LITERATURE

- (1) EUGENE OBACH.—Cantor Lectures on Gutta-percha, 1898, p. 6.
- (2) KEMP AND MULLER.—“Iodine Value of Rubber and Gutta-percha Hydrocarbons,” Bell Telephone System Technical Monograph B, 779.
- (3) DEAN.—“Heat Treatment and Polymorphism of Gutta-percha and Balata,” *Trans. Inst. Rubber Ind.*, 8, 25 (1932).
- (4) TSCHIRCH.—“Die Harze und die Harzebehälter,” 1906, p. 893.

Gutta-percha is the name given to a gum originally obtained from various trees of the genus *Sapotaceæ*. The variety yielding the original gutta is called *Isonandra Gutta*. The trees are now more commonly known as *Dichopsis Gutta*, or *Palaquium Gutta* (1). *Dichopsis Gutta*, found only in the Malay Archipelago, is now very rare, although preserved by certain plantations. Sundry other trees are utilised in the commercial production of gutta-percha, but only that obtained from the species *Palaquium*, notably *Palaquium Oblongifolium*, is comparable in quality with *Dichopsis Gutta*.

Jungle gutta-percha, obtained mainly from Malaya and Borneo, is usually prepared by felling the trees and stripping the bark. The gum, which coagulates rapidly, is boiled in water and moulded into blocks or shapes.

Plantation gutta-percha is obtained by plucking the trees of their mature leaves, which are ground in mills. The mash so formed is treated with water at about 70° C., then plunged into cold water, when the hot gutta floats to the surface, and the leaf debris, water-soaked, sinks to the bottom. After pulverising and sieving, the material is boiled in water and pressed into blocks.

In either case the raw product consists of gutta-percha hydrocarbon, resin, dirt, and moisture.

Chemically the hydrocarbon has the empirical formula  $C_5H_8$  and is isomeric with rubber. At ordinary temperatures it is hard and tough, but softens on warming until at 100° C. it is plastic and slightly sticky and can readily be moulded into shapes. On cooling, it quickly reverts to its original state, this process being capable of continuous repetition. Gutta-percha is thus an example of a thermoplastic material.



It is soluble in most aromatic hydrocarbon solvents at room temperature, but dissolves in saturated straight chain solvents only at elevated temperatures. Most chlorinated hydrocarbons are very effective solvents, but esters have only partial or no solvent action.

Gutta hydrocarbon is attacked by strong sulphuric and nitric acids, and forms nitroso compounds similar to those formed by rubber. It is, however, extremely resistant to attack by hydrofluoric acid and this has led to the use of gutta-percha as a storage container for this acid. Solutions of acids, alkalis, and salts have but little effect, although in the presence of oxygen they may cause rapid oxidation.

Gutta-percha, especially when pure, is very liable to oxidation; but anti-oxidants of similar type to those used in rubber are effective. Oxidation is catalysed by ultra-violet light, and the hydrocarbon is usually stored in the dark. The attack of oxygen proceeds particularly rapidly in solution, and solvents of minimum oxygen absorption are preferred.

Unsaturation is the same as in rubber, viz., one double bond per  $C_5H_8$  radicle (2). The density of the hydrocarbon is about 0.95 and varies slightly, depending on the source. It is also dependent on the physical condition of the sample; it has been shown that this is due to polymorphism (3).

The resins of gutta-percha vary with the sample and have been described by Tschirch (4).

**Manufacture and Uses.**—The raw gutta-percha, after washing by mastication in hot water, is strained and dried. It is then blended to achieve uniformity and to attain optimum properties.

The excellent water resistance and electrical properties of gutta-percha ensured that its main use was in submarine telegraph cable, and until recently it was unsurpassed in this field.

Other uses are adhesive tissue, moulded articles for use in hydraulic systems, and chemically resistant vessels.

The best, *i.e.*, plantation, grades of gutta-percha, after subjection to a solvent process to remove resin, may be bleached to give a tough, pure white product much in demand as a cover for golf balls.

**Balata.**—Balata is similar in many ways to gutta-percha. It is obtained from the tree *Mimusops Globosa*, of the *Sapotaceæ* family, by heating the latex until it coagulates and then pressing into blocks, or by evaporating the latex to give thin sheets. Countries of origin are mainly the Guianas, Brazil, and Venezuela.

The hydrocarbon is similar to that of gutta-percha and may be used for similar applications. The resins, which differ somewhat from those of gutta-percha, have been described by Tschirch.

**Shellac.**—This material is described on page 346 and page 485.

**Rubber.**—This material is described on page 353.

**Natural Resins.**—These are described on page 345.

## PHENOLIC RESINS

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## History of Phenolic Resins

The synthetic materials produced by condensing phenols with aldehydes were the first resinous products to be produced commercially from low molecular weight materials. Since 1910 their annual production has grown enormously and they are still one of the most important members of the plastics industry despite the rapid growth of several other plastics.

Baeyer, in 1872, first noticed that phenol and aldehydes reacted together to form resins. Little interest was manifested in these resins until formaldehyde was manufactured industrially in 1890 with a reduction in its price. Several chemists produced hard infusible materials from phenol and formaldehyde, and then Lederer and Manasse showed that phenol and formaldehyde reacted in an alkaline medium to form ortho- and parahydroxybenzyl alcohol, *e.g.*, phenol and aqueous formaldehyde in aqueous solution in equimolecular proportions are treated with dilute caustic soda at room temperature and the reaction products extracted with ether after neutralisation. Steam distillation of the extract will remove the unreacted phenol.

**Early Industrial Developments.**—Early patents introduced phenolic resins as shellac substitutes and moulding compositions for electrical insulation.

Blumer condensed phenol, formaldehyde, and tartaric acid together, and dissolved the product in alcohol. The solution was used as a spirit varnish.

Smith’s ebonite substitute was made from phenol and formaldehyde with hydrochloric acid as catalyst in a solvent diluent such as amyl alcohol to moderate the reaction. The solvent was then removed at 100° C. after casting the solution in moulds.

**Fast Curing Mouldings.**—All the early workers were faced with the problem of controlling the rather violent reaction between phenol and formaldehyde. It was Dr L. H. Baekeland who, between 1905 and 1911, solved the problem of making, under controlled conditions, quick-curing mouldings which were non-blistering and strong. He showed that acids and bases were catalytic in the reaction and that consequently only very small quantities were required. Previous workers had used equimolecular proportions. He showed that permanently fusible resins could be produced from phenol and formaldehyde when small proportions of acid catalysts were used and that these could be dissolved in common solvents. He termed these resins Novolaks, a name which is still used to-day. When an alkaline catalyst such as ammonia was used, Baekeland found



that a different type of resin was formed—in fact, he found that, by careful control, three distinct resins could be obtained. He called these resins A, B, and C. He found that resin A was a liquid or a solid, soluble in alcohols, ketones, ethers, esters, chlorinated hydrocarbons, etc. On heating resin A it passed into resin B, an infusible solid which, however, did become rubbery on heating; this material was insoluble in the above solvents, but swelled slightly in alcohol and acetone. On further heating, the B resin was converted into C resin, a hard infusible material insoluble in all solvents.

When this progressive change in these resins had been realised, Baekeland used fillers such as wood flour, cotton, and asbestos to improve the strength of his resins, which were inclined to be brittle in the infusible state.

Another investigator, Lebach, a contemporary of Baekeland, was first to show that the soluble resins could be converted into the insoluble type by the action of further quantities of catalyst and formaldehyde. He also showed that the phenol-formaldehyde resins could be hardened by the action of heat much more quickly if they were first rendered acid. Lebach also pioneered the production of light-coloured phenol-formaldehyde resins by the use of excess formaldehyde. Lebach called the first condensation products (*i.e.*, those soluble in common solvents and fusible) resols, while he called those hardened by further heat but still fusible, resitols. The final infusible and insoluble product he called a resit. These correspond to the resins A, B, and C above.

**Recent Developments (1910–1949).**—Soon after 1910, modified resins began to make their appearance. Modified resins were first introduced in order to render them soluble in drying oils. Rosin was used for this purpose.

In about 1930 synthetic substituted phenols were introduced in order to make oil-soluble resins.

In 1935 the ion exchange properties of phenol-formaldehyde resins were discovered and they have recently been found useful for water softening. (See pp. 631–2.)

### The Theory of Formation of Phenol-Formaldehyde Resins

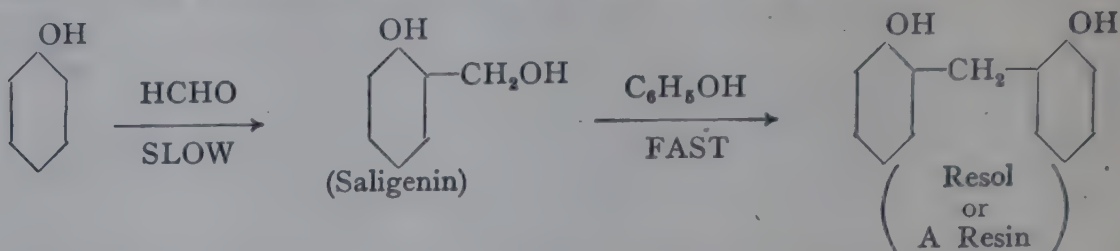
The essential chemical process during the formation of phenol-formaldehyde resins is the heating together of phenol and formaldehyde, or more generally a phenol and an aldehyde, until condensation has taken place with the liberation of water. This is distilled off, leaving the residual resin to set on cooling. The initial condensation between phenol and formaldehyde is too slow for commercial usage, and catalysts are always used. Acid catalysts are used for the manufacture of two-step, novolak, or B resins which are permanently fusible, while alkaline catalysts are used for the manufacture of the thermo-setting (heat hardenable) one-step or resol resins (A resins). Whether the one-step or two-step resins are formed, the initial reaction is the same in both cases—the phenol forms an addition product with the formaldehyde to form phenol alcohols. These phenol alcohols may then condense with one another or with more phenol and so on, building up complex materials. In both resols and novolaks the size of the molecules is relatively small compared with those of the vinyl type resins (see under **Thermoplastics**).

The chemical nature of resols and novolaks has been the subject of considerable controversy in recent years and many weird ideas have been put forward. Probably the following is the present majority view:—

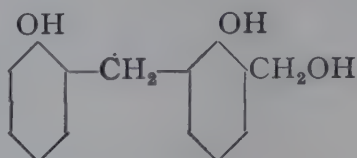
Resols are converted into larger molecules on heating without the use of hardening agents and are thought to contain reactive methylol groups in the molecule which facilitate condensation of the resols on heating to form larger molecules.

Novolaks are thought to have no reactive methylol groups in the molecule and do not react with one another on heating without hardening agents.

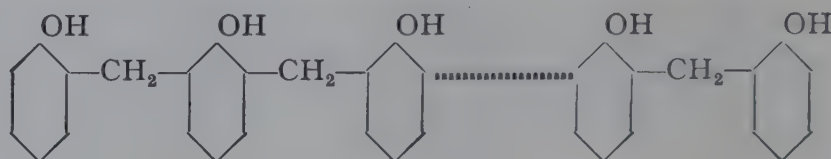
The use of acid and alkaline catalysts cause the following differences in the condensation products and speed. Acid catalysts cause slow formation of phenol alcohols but cause these phenol alcohols to condense quickly with phenol to form diphenylol methanes. These particular condensation products are found in the novolaks. Their formation is depicted by the following scheme:



The resol then condenses with a further quantity of formaldehyde to form a compound of the nature



This compound then condenses into resitol or B resin in the presence of free phenol:



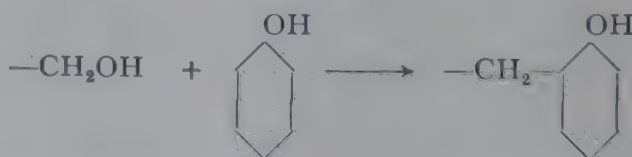
again with the elimination of water.

These novolaks, resitols or B resins are polynuclear phenols of various chain lengths from 2-13 benzene rings. As they contain no reactive methylol groups they do not condense on heating, but if they are heated with formaldehyde they are cross-linked by methylene bridges and form a hard infusible product.

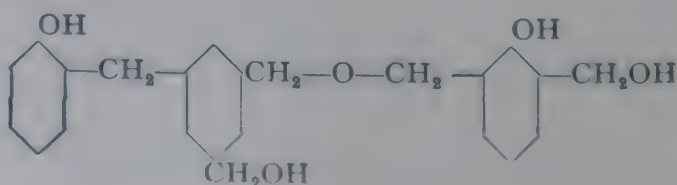
When alkaline catalysts are used, however, for the condensation of phenol and aldehydes the initial addition reaction is faster than the subsequent condensation reaction (in contrast to the case where acid catalysts are used), and because of this phenol alcohols are predominant in the initial stages of the reaction. The reactive  $-\text{CH}_2\text{OH}$  groups in these phenol alcohols either condense amongst themselves, forming ether links thus:



or they condense with a reactive hydrogen atom in a benzene nucleus in the ortho or para position to the  $-\text{OH}$  of the phenol, thus:



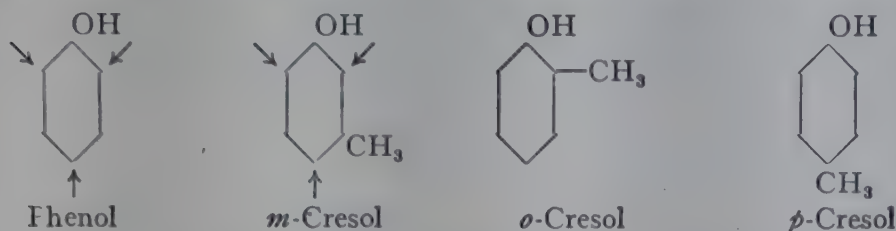
forming a methylene bridge as in the novolaks. These materials may be liquid or solid, depending upon the degree of this condensation. In the liquid novolaks the number of benzene nuclei may average two, while in the solid novolaks it may average four, *e.g.*,





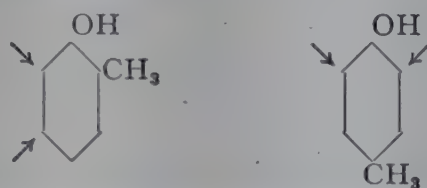
The uncondensed phenol alcohol groups in the above formula cause the cross-linking that occurs when a novolak is heated or treated with acid.

**Functionality.**—When phenol or phenolic materials are condensed with the aid of formaldehyde and a catalyst, the condensation reactions normally take place in the ortho or para positions in the benzene nucleus only (with respect to the hydroxyl group). Now consider the molecules of phenol, *m*-cresol, *o*-cresol and *p*-cresol.



Phenol and *m*-cresol have a functionality of three because the condensation reactions may take place at any of the ortho or para positions, with regard to the OH group. All these positions are free in both materials as indicated by the arrows.

Now in the case of *o*- and *p*-cresol we have a functionality of two as shown by the arrows in the following formulæ:—



As the condensation reactions may only take place at an ortho or para position, it is seen that there are only two such positions with respect to the OH group in both these materials.

It was Kienle who first pointed out that unless the functionality of one of the two reactants in the condensation is at least three, cross-linking was impossible to the extent where the resins became thermo-setting. As formaldehyde only has a functionality of two, the phenol used with it must have a functionality of three to obtain a thermo-setting resin. That is to say, the phenol must have the two ortho positions and the para position free. Every rule has its exceptions, but there are relatively few cases when we find thermo-setting resins derived from ortho or para phenolic materials. It is thought that the cause of hardening with these materials is a reaction between the hydroxyl groups of the phenols.

We find occasionally that very large substituents in the meta position in a phenol are the cause of failure to harden. This is explained as a steric hindrance. The large group covers the ortho position or the para position or both.

**The Thermo-setting Process.**—When resols (A-stage resins) from phenols with three reactive positions are heated to a temperature of 130° C. they melt and froth due to the liberation of water vapour which is a product of the condensation process. A rubbery product results (B-stage resin or resitol) which is insoluble in common solvents but which will still swell in acetone. Further heating converts this rubbery material into the C-stage resin or resit. The structure has gradually changed from the low molecular-weight polyalcohols of the resol stage by way of partly linked large molecules in the resitol stage to the intensely cross-linked, three-dimensional structure of the resit stage.

In the case of low molecular weight liquid resols this change may be brought about by the addition of a small quantity of a strong acid without the application of heat. The condensation of methylol groups thus initiated liberates sufficient heat to complete the reaction unless this heat is removed too quickly. A larger proportion of the acid catalyst will cause hardening even without the necessity



to maintain the liberated heat. Use has been made of this phenomenon in the manufacture of cold-setting adhesives and casting materials.

### The Industrial Manufacture of Phenol-Formaldehyde Type Resins

The following raw materials are used for the manufacture of these resins:

Phenol (99.9 per cent.) and phenol (90 per cent.) ortho-cresol (10 per cent.) mixture containing traces of pyridine bases.

Cresol (40–55 per cent. meta), (60–45 per cent. para) containing traces of pyridine bases, ortho-cresol, and xylenols.

Xylenol.

Formalin 37 per cent. stabilised with methanol.

Hexamethylene tetramine.

The phenols are usually obtained from coal-tar distillation although recently phenol has been synthesised from benzene as a commercial proposition, especially as benzene is now obtainable from catalytic cracking of petroleum fractions.

Formaldehyde is made commercially by the catalytic combination of carbon monoxide and hydrogen.

Pure phenol is preferred for phenolic-resin manufacture because, being of constant composition, a resin with fairly consistent properties can be manufactured from it. When 90 per cent. phenol is used, the varying proportions of ortho-cresol and pyridine it contains give a variable product. Another source of variability in the product is the formaldehyde. This, in the form of formalin, may contain various amounts of free formic acid, methanol and polymers of formaldehyde, all of which affect the reactivity of the solution in some way or another. Batch variations have been reduced to the minimum recently by the huge quantities of both phenol and formaldehyde manufactured, resulting in large batches and thus less variation by reason of the longer period each batch is in use.

Oil-soluble resins are manufactured by the use of synthetic paraphenols; for example, para-tertiary-amyl-phenol, para-tertiary-butyl-phenol.

Other aldehydes such as acetaldehyde and furfuraldehyde are sometimes used for the manufacture of phenolic resins for various high-voltage electrical purposes as they have good resistance to tracking. Furfuraldehyde resins are more stable at temperatures of the order of  $230^{\circ}\text{C}$ . Furfuraldehyde is a raw material obtained quite cheaply from oat husks and other similar material.

The manufacturing processes required for phenolic resins are rather dependent upon the use for which the resin is required. The products generally made comprise:

(a) Ground solid resins—novolaks for bonding and for the manufacture of moulding material.

(b) Liquid resins—partially dehydrated resols mainly for bonding agents.

(c) Varnishes which are generally solutions of the solid or liquid resins in ethyl alcohol, butyl alcohol or acetone or mixtures of these. These varnishes are used for paper and fabric impregnation, and surface coating for various industries including the electrical industry.

(d) Oil varnishes which consist of the oil-soluble type of phenolic resin dissolved in a drying oil and thinned with a solvent. These are used for surface coating and coil impregnation.

(e) Lacquers which are solutions of resols in a carefully blended mixture of solvents which evaporate at such a rate that a good film is left. These are used for surface coating.

### Plant used for the Manufacture of Phenol-Formaldehyde Resins

Nearly all the manufacture is by batch processes although continuous processes are also used. In the batch process the plant consists of a large still with a



dished or hemispherical top. The still is provided with means of steam heating or water cooling. Copper is often used for the manufacture of the still, but mild steel, iron, stainless steel or nickel are used. The choice of metal is governed by the type of resin to be made. Copper, nickel, and stainless steel are suitable for the novolaks, while mild steel, iron or copper are used for the resols when colour is not important. Where colour is important, stainless steel is always used.

A stirrer is fitted to the top of the still through a gland. A condenser is also connected to the top of the still. All these accessories are made from the same metal as the still. The stirrer is of the anchor type which sweeps closely to the sides of the vessel. A charging line for raw materials also enters the still by the top, and on the top is also fitted a sight glass to view the contents of the still. A manhole for cleaning purposes, a pressure safety valve, pressure and temperature recording devices and condenser complete the fittings at the top of the still. At the bottom of the still is an outlet for the finished reaction mixture which is run into trays and cooled in the case of novolaks. In the case of resols the cooling must be rapid and in thin layers to prevent further polymerisation—*e.g.*, one inch.

### Manufacturing Procedure

**Resols.**—Phenol-formaldehyde in slight molecular excess and alkaline catalyst about .2 per cent. are charged into the still and the valves arranged so that refluxing takes place. The temperature is raised gradually until the reaction begins. The temperature is then kept below  $100^{\circ}\text{C}$ . by means of water cooling until the reaction is complete. The catalyst is often neutralised at this stage, followed by vacuum distillation of the water present in the reaction mixture at about 25 inches mercury and a temperature somewhat less than  $100^{\circ}\text{C}$ .

When nearly all of the water has been distilled from the resin mixture the temperature is allowed to rise. Samples of the reaction mixture are taken very frequently and tested for melting-point, degree of polymerisation, and hardness until the end point has been reached.

The resin is then run out from the valve at the bottom of the still and cooled rapidly if a solid resin is required. This is then ground. If a varnish is required, the alcohol may be run into the still after slightly cooling the resin, and the solution run out after thorough stirring.

The walls of the still require to be cleaned thoroughly from time to time as they become coated with a hardened layer of the resin due to the fact that it is highly temperature-sensitive.

**Casting Resins.**—Casting resins are manufactured by using a large excess of formaldehyde with caustic soda as catalyst at a temperature of  $60^{\circ}$ – $80^{\circ}\text{C}$ . This encourages the formation of hydrophilic phenol alcohols of low molecular weight. After the reaction is completed the catalyst is neutralised with lactic acid which has a highly soluble sodium salt which will not crystallise out. After vacuum evaporation the resin may be cast directly into moulds and cured at temperatures of the order of  $75^{\circ}\text{C}$ ., or may be stored as a liquid and cured as required by heat or by the use of an acid accelerator.

**Novolaks.**—Phenol, formaldehyde solution and acid catalyst are charged into the still and the temperature gradually raised until the mixture boils. As the reaction is strongly exothermic, the still must be cooled to maintain gentle boiling at  $100^{\circ}\text{C}$ . After a few hours the water is allowed to evaporate at atmospheric pressure until the temperature rises above  $100^{\circ}\text{C}$ . and the resin becomes clear. This temperature rise is often taken to  $150^{\circ}\text{C}$ ., and often vacuum is also applied in the later stages to remove unreacted materials and the last traces of water. The resin is then discharged into trays.

**Subsequent Treatment of Resols and Novolaks.**—Most resols are used in solution which is made in the stills before their discharge. Solid resols have



a melting-point of  $40^{\circ}$ – $50^{\circ}$  C. and cannot easily be ground in warm weather owing to caking.

Novolaks have a melting-point of  $70^{\circ}$ – $80^{\circ}$  C. and are easily ground with hammer mills.

**Applications of Phenolic Resins.**—These may be divided into six classes: (1) moulding and casting resins, (2) adhesives, (3) impregnation resins, (4) surface coating resins, (5) ion exchange resins, (6) miscellaneous modified resins.

**1. Moulding compositions.**—Phenolic resins are still the most important moulding compositions in the plastics industry. They form durable materials which are chemically resistant to a wide range of reagents. Probably most important, their heat resistance is greater than many common materials and change of shape with age is negligible. Phenolic resins are resistant to oils, grease, and all common solvents. They will also withstand weak mineral acids and alkalis and all organic acids. Fillers may be introduced to improve their properties in one way or another.

The electrical industry has used phenolic resins now for many years. For low-frequency and direct-current application, phenolic resins have just the right combination of properties required: high insulation value, fairly high resistance to heat and inflammability, high resistance to water, oils, and atmospheric deterioration, and finally, most important, the property of accurate moulding to enable them to be fitted to metal parts of electrical apparatus.

When phenolic resins are used for moulding, their inherent brittleness necessitates their being used in conjunction with reinforcing fillers such as cotton, wood flour and such materials. Asbestos imparts superior heat resistance.

Carefully hardened resins containing dyes but no fillers are moulded into decorative handles for umbrellas and artificial jewellery. Liquid resins with or without fillers have been used recently for various engineering tools such as jigs and dies by curing them in moulds at slightly elevated temperatures.

Expanded phenolic resins are now being extensively used for heat and sound insulation. Densities down to 0.1 gr./c.c. are obtained. The expanding action is obtained by heat decomposable materials, such as sodium bicarbonate which liberates carbon dioxide, or organic materials which liberate nitrogen.

A relatively new application of phenolic resins utilises the pulp-preform method. A pulp of a cellulosic material is made with water in a paper-beater and then mixed with an emulsion of the phenolic resin with water. The pH is then adjusted to cause the phenolic resin to be precipitated on to the cellulosic material. A preform is now made, squeezing out much of the water, the rest of which is removed under vacuum and moderate heat. The dry preform is then hot moulded, and it is found that much lower moulding pressures are required than with normal mechanically loaded materials. Very high impact strengths are obtained, and lower resin contents are possible than with material which are moulded in the ordinary way. Wall boards are manufactured by similar method.

Brake linings are made by incorporating asbestos filler with only 10 per cent resin. Grinding wheels are made by incorporating an abrasive grit by a wet or dry process and then moulding at elevated temperatures. Phenolic resins have replaced glue in many abrasive papers.

**2. Adhesives.**—Phenolic adhesives are renowned for their heat resistance. They are largely used to-day for cementing the glass into the caps of electric light bulbs and radio valves. A mixture of novolak with hexamethylene-tetramine (a condensate of formaldehyde and ammonia) and ground marble is generally used. Shellac is often added to the mixture for radio valves, and a longer heating time at a lower temperature is given.

Plywood is often manufactured by using a piece of tissue paper impregnate



with an alcoholic solution of a resol for the layer of adhesive between the layers of wood. These are pressed at approximately  $150^{\circ}\text{C}$ .

Adhesives for setting the bristles in brushes are now often made from acid-hardening cements cured at about  $60^{\circ}\text{C}$ ., which avoids damage to the bristles from higher temperatures.

Acid-proof cement for setting tiles in chemical plant is made from similar materials. Powdered silica is often used here for a loading material, and an aromatic sulphonylchloride is often used as the catalyst which, on slowly hydrolysing, liberates sulphuric and hydrochloric acids.

The whole field of phenolic adhesives is so widespread owing to their durability, from all aspects, in comparison with the older adhesives.

**3. Impregnation.**—Large quantities of phenolic resins of the resol type dissolved in alcohol are used for plywood manufacture by impregnating paper as mentioned above. In addition, wood is now impregnated by a vacuum technique followed by high pressures while immersed in an alcoholic solution of a resol. The wood is dried at temperatures of the order of  $100^{\circ}\text{C}$ . and the resin cured under pressure at  $125^{\circ}\text{C}$ ., giving a wood of specific gravity of the order of 1.3 containing 40 per cent. of resin. Planks of impregnated wood may be "plied up" and cured into blocks. Such wood is resistant to warping and to the effects of atmospheric deterioration.

Similar impregnation is carried out with electrical apparatus such as coils, armatures, and transformers—vacuum, moderate heat, then pressure and curing heat.

Porous machine castings are now filled with phenolic resin by a vacuum technique and cured into a casting quite as good as a non-porous one.

**4. Surface coatings.**—For corrosion resistance, many metal parts are now coated with a phenolic spirit lacquer which is then cured to form a heat- and chemical-resisting film. Examples of this practice may be noted in the canning industry where nowadays most cans are lined with a phenolic resin although they are not resistant to some fruit acids; the wire industry, the razor-blade industry, food industry plant, and any application where a tough corrosion-resistant coat is required. Very thin coats are generally applied by a roller coating machine followed by curing at a temperature of  $200^{\circ}\text{C}$ .

Dispersions of phenolic resins are now used in the paint industry often for primer paints on account of their quick-drying properties. They are made from ground semi-cured phenolic resins dispersed in a drying oil in which they form a complex due to their moderate solubility. These mixtures are taken up in a volatile solvent and dry mainly by evaporation. They then have high weather resistance.

**5. Ion exchange resins.**—Adams and Holmes discovered, in 1935, that there was a reversible exchange of ions between hardened phenolic resins and solutions in which they were immersed. This property is now being used extensively for purifying water, particularly in America.

**Anion exchange resins.**—These are resins of the aniline or *m*-phenylenediamine type, condensed by means of excess formaldehyde. This produces an insoluble structure containing many amino groups. The action of these resins is due to the active amino groups of the insoluble macromolecular structure. Other groups are sometimes added to intensify the action of the amino groups. These amino groups usually act as basic groups and merely absorb acids to form salts but sometimes they act as true anion exchange groups, replacing the anion of a neutral salt by hydroxyl groups. Regeneration may be accomplished by treating the resin with aqueous caustic soda. The action of these resins is slightly improved by rise of temperature. They are mainly used for water softening in conjunction with cation exchange resins as described below under this head. Other uses of anion exchange resins include the removal of ionic impurities from



non-polar organic materials; for example, metal ions from sugar and formic acid from formaldehyde. They are also used to remove valuable metals from waste liquors. Metals may be estimated stoichiometrically in this way.

**Cation exchange resins.**—These resins are made from polyhydric phenols such as quebracho or catechol-tannins and phloroglucinol by condensation with excess of formaldehyde. At least two molecular proportions of formaldehyde to one of the phenol are used to ensure that a very insoluble highly cross-linked macromolecular structure results. As in the anion exchange resins, active groups may be introduced to increase the anion exchange properties of the resin. Methylene sulphonie-acid groups may be introduced by the addition of sodium sulphite during the condensation of polyhydric phenols and excess sodium sulphite, or, alternatively, phenols containing sulphonie or carboxyl groups may be used with excess formaldehyde. For cation exchange with solutions of different acidities it is found that some groups are more effective than others, *e.g.*,—

—SO <sub>3</sub> H	for very low pH solutions,
—CH <sub>2</sub> SO <sub>3</sub> H	for low pH solutions,
—COOH	for neutral solutions,
—OH	for high pH solutions.

It is, however, not advisable to add too many hydrophilic groups, as the resins then become appreciably soluble and swell in water. It is necessary to draw a compromise between efficiency of ion exchange and solubility.

In contrast to the behaviour of anion exchange resins, that of cation exchange resins is always a true ion exchange reaction. The cations in the resin may be replaced by sodium or hydrogen according to whether the resin is regenerated by means of hydrogen-chloride or sodium-chloride solutions.

**6. Miscellaneous modified resins.**—Various materials are introduced into phenolic resins for specific purposes.

Toxic materials such as arsenic and mercury compounds are introduced for antifouling paints. Lead compounds are introduced for radio-opaque mouldings.

The carboxyl groups in the benzene nucleus may be esterified by means of glycerol to give softer resins.

In fact, any material which has an affinity for hydroxyl groups may be used to modify a phenolic resin.

## UREA- AND MELAMINE-FORMALDEHYDE RESINS

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### History

This class of resin results from the reaction of an aldehyde (usually formaldehyde) with acid amides such as urea, thiourea, and melamine.

Hans John, in 1918, excited commercial interest in urea formaldehyde. He prepared resinous materials by reacting urea with excess of formalin and found the various solutions thus obtained useful as adhesives and impregnants. In the meantime Goldschmitt and Neuss in Germany, and Ellis in America, were working on moulding compositions. In Britain the British Cyanides Co. Ltd. (now British Industrial Plastics) began the manufacture of thiourea and discovered its reaction with formaldehyde.



The light colour of resins manufactured from urea and its derivatives caused most interest in their manufacture. The early manufacturers found that successful resins could only be produced by using mixed thiourea and urea with excess formaldehyde. Either used alone did not then give a good moulding composition.

A use for urea resins which spurred further development was their incorporation in fabrics to give a non-creasing effect. This process was developed by the Tootal Broadhurst Lee Co. Ltd.

In 1935 Henkel patented the production of resins obtained from the condensation of aminotriazines with formaldehyde. Melamine resins followed from this discovery. They combine the light colour of urea resins with the heat resistance of phenolic resins.

A full account of the history and references to patents is given in the Plastics Institute monograph mentioned above.

### Raw Materials for the Manufacture of Urea-Formaldehyde Type Resins

These are urea, thiourea, melamine and formaldehyde.

**Urea.**—This is produced by the reaction of carbon dioxide and ammonia at about 170° C. and 200 atm. in an autoclave.

Ammonium carbamate is first formed, which then decomposes to give urea and water:



The reduction of volume favours high pressures for the reaction by Lechatelier's Rule. Up to 60 per cent. conversion is obtained, and unused ammonia and carbon dioxide are recycled.

**Structure of Urea.**—To obtain a true picture of the building up of urea-formaldehyde resins, it is necessary to understand the structure of urea itself. There has been some controversy over the constitution of urea. The popular conception is a simple carbamide formula,  $\text{NH}_2\text{—CO—NH}_2$ , but E. A. Werner, in his monograph "Chemistry of Urea," produces evidence that in aqueous solutions urea reacts as an equilibrium mixture of the structures:



**Thiourea.**—This is produced by the reaction of hydrogen sulphide upon a solution of cyanamide or from ammonium thiocyanate, a by-product of the production of coal gas.

In the hydrogen sulphide process, calcium cyanide is suspended in water, and lime removed by precipitation with  $\text{CO}_2$ . Ammonium sulphide is then added in excess.

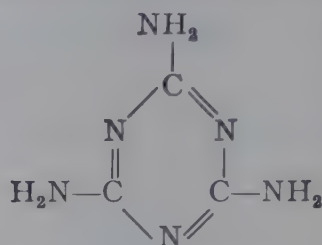
In the ammonium thiocyanate process, the liquor containing the salt is concentrated and finally fused at 145° C. when a 25 per cent. conversion to thiourea is obtained:



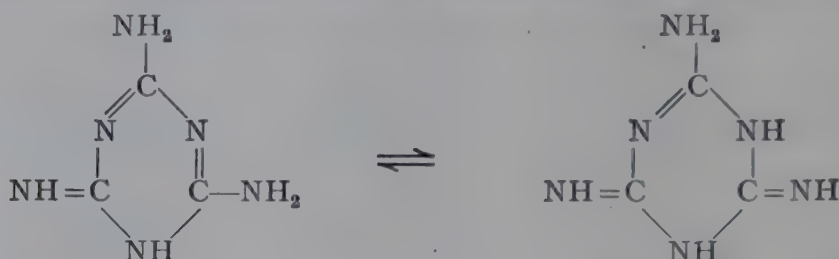
From the equation it is seen that increased pressure will not favour the reaction either way. Nor has increased temperature or the presence of catalysts any pronounced effect. Only 25 per cent. yield is obtained, and the converted material is extracted and recrystallised.

Again, as with urea, E. A. Werner finds that the formula  $\text{NH}\cdot\text{C}(\text{SH})\cdot\text{NH}_2$  conforms with the reactions of thiourea better than the formerly accepted  $\text{NH}_2\cdot\text{CS}\cdot\text{NH}_2$ .

**Melamine.**—This is produced by the polymerisation of cyanamide. Calcium cyanamide is extracted with water, and lime impurity precipitated by means of carbon dioxide. The solution is then heated in the presence of alkali (ammonia), thus polymerising the cyanamide to dicyanamide. The solution is then concentrated for crystallisation, and the dicyanamide further polymerised either by heating under pressure with ammonia or by heating in the presence of guanidine salts. This latter method is the subject of a patent by British Industrial Plastics Ltd. (B.P. 533,426). Melamine has been allotted the formula:



but its reactions seem to suggest that it is in the following equilibrium:—



**Formaldehyde.**—This is manufactured by the controlled oxidation of methyl alcohol by passing the latter admixed with air over heated copper coils. The formaldehyde produced is condensed together with the water also produced, giving commercial formalin:



It is found that the presence of unchanged methyl alcohol improves the stability of the formalin produced, and further quantities are often added for this purpose.

### The Chemistry of Urea-Formaldehyde Reaction.

It is found that at normal temperatures the following reaction takes place between urea and formaldehyde:



Monomethylol urea is precipitated from a neutral solution of equimolecular proportions of urea and formaldehyde after a few days. The reaction may be speeded by gentle heat. (The formalin may be adjusted to pH 7.5 by means of caustic soda and the urea dissolved in the solution.)

When the above reaction is repeated, using two molecules of formaldehyde to one of urea and a temperature of 60° C., dimethylol urea is obtained:



These methylol ureas will condense to yield products of increasing infusibility and insolubility. The dimethylol ureas especially produce resinous products,

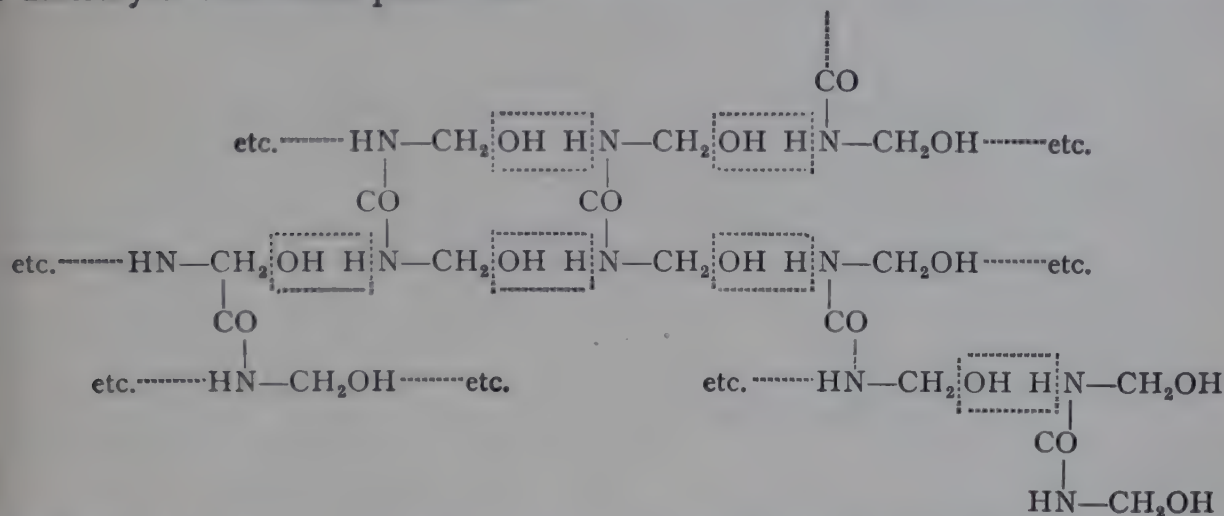


while those from the monomethylol ureas tend to be amorphous. The presence of both compounds are apparently necessary for resin formation.

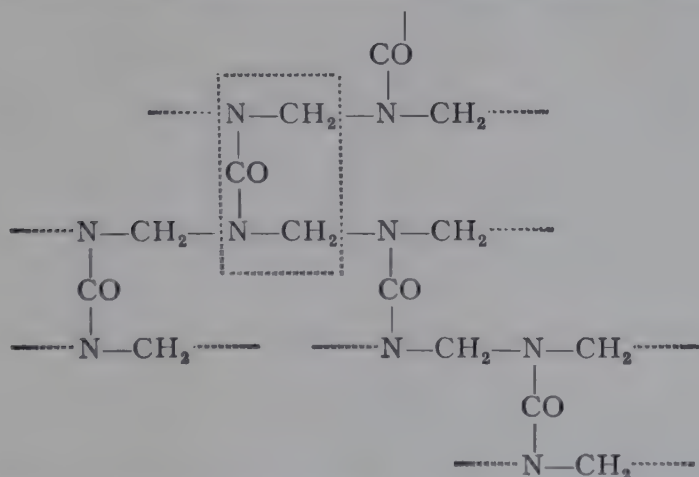
When dilute acids are present, urea and formaldehyde condense to form methylene urea.



Little controversy exists with regard to the above reactions, but the later reactions giving the thermo-hardened product are rather uncertain. A three-dimensional structure appears to be formed. Walter and Gaving suggest that condensation of dimethylol urea takes place thus:



Redfern has suggested polymerisation of dimethylene urea thus:



It is not possible to record here the many views on and researches into this reaction. The condensation product is profoundly dependent upon three factors:

- (1) The molecular ratio of the reactants.
- (2) The pH of the solution (the lower the pH the faster the reaction).
- (3) The time and temperature of the reaction.

### The Commercial Preparation of Urea-Formaldehyde Resins

Urea-formaldehyde moulding powders are prepared in two stages:

**Stage 1.**—Neutralised formalin and urea in the molecular ratio of 1.6 : 1 are treated with a small quantity of ammonia and allowed to stand for a few hours in the cold. After this time a clear solution containing 60 per cent. of the resin is obtained. This solution is then mixed with about 30 per cent. of its

weight of cellulose filler at 60° C. in an internal mixer such as a Werner-Pfleiderer. The damp product is spread in trays and dried at about 80°–90° C. Then a small quantity of zinc stearate lubricant, colouring matter, and 1 per cent. of a solid acid catalyst, *e.g.*, cinnamic acid, are added and the whole ground in a ball mill.

**Stage 2.**—The moulding powder is compression-moulded when the acid catalyst causes hardening at a temperature of about 140° C. for  $\frac{1}{2}$  to 12 minutes, depending on the thickness.

The type of cellulose filler used affects the appearance of the finished article. When paper is used, the resins tend to be translucent and this is a property with some advantages. When wood flour is used a more opaque product is obtained. As much as 85 per cent. of cellulose may be added to the resin in the mixer. It is found that the cellulose enhances the stability and ageing characteristics of the resin.

**The Properties and Uses of Moulded Urea Resins.**—Urea resins possess a number of useful characteristics. They are resistant to oil, grease, weak alkalis, weak acids, alcohol and other solvents. They are resistant to oxidation and are very hard and resistant to abrasion. They have high tensile strength. The moulded products are inert and have no taste or smell. They are therefore largely used in tableware. A complete colour range is available in contrast to phenolic resins. Urea resins are not so heat-resistant as phenol-formaldehyde resins, but they are good electrically and do not suffer from "tracking" as do some phenolic resins.

In addition to their use in tableware, moulded urea resins are used for electric-light fittings and shades, bedside telephones, bottle caps, cosmetic containers, and for any purpose where an attractive rigid material is required.

**The Properties and Uses of Solutions of Urea Resins.**—Since the reaction between urea and formaldehyde may be stopped at any stage from a colourless liquid through a rubbery solid to a solid infusible material, it is not surprising that uses have been found for these alternative forms of the condensate.

The initial solution is widely used as an impregnant for paper, cloth and asbestos, and these materials may then be compressed into sheets and tubes. Wood flour and mineral fillers are also often incorporated.

The resin solution may have its hardening action accelerated or retarded by various ingredients. Acceleration of the action is brought about by a hydrogen ion donor, *e.g.*, any acid or acid-reacting material. Alternatively a hydrogen ion acceptor, *e.g.*, an alkaline-reacting material, will retard the setting action. Quick-setting cements are frequently manufactured by using the principle of acid hardening.

Aqueous solutions of urea-formaldehyde resins are used very largely for stiffening fabrics by soaking them in the solution, drying at 100° C., and pressing. The pioneers in this field were the Tootal Broadhurst Lee Company of Manchester, and their non-creasing fabrics are well known. In the most interesting product the surface coating of resin is removed and the suppleness of the material is restored, leaving only the non-creasing property.

**Urea-Formaldehyde Adhesives.**—Urea-formaldehyde adhesives are probably the most important used to-day. They may be applied cold or hot. They are resistant to moisture and are unaffected by moulds, corrosive materials and elevated temperatures. Their use is enormous in plywood manufacture and in aircraft construction.

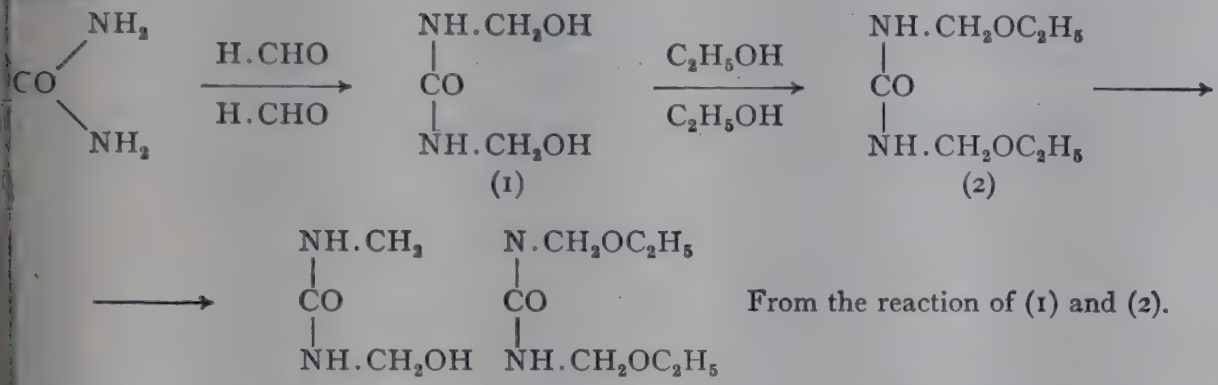
A concentrated aqueous solution, together with up to 300 per cent. by weight of wood-flour filler, is mixed with an acid hardener just before use. Where a gap-filling cement is not required, the proportion of filler may be reduced. Fillers (which are useful in reducing the contraction of the cement after setting) may include wood flour, ground phenol-formaldehyde resins, silica and plaster of Paris. Proprietary cements are Kaurit Glue W, in Germany, and Beetle Cement W.



Urea-formaldehyde cements are used in conjunction with a hardener supplied separately and mixed with the resin solution just before use. Alternatively the hardener may be applied to one surface to be joined while the resin solution is applied to the other. As stated above, the hardener is a dilute acid—the stronger the acid, the quicker the hardening action.

As the resin solution will not keep for long, a powdered urea formaldehyde has been brought on to the market which need only be dissolved in water to give a solution that can be used in the usual way. The powder will keep for over a year.

**Urea Resins for Lacquers and Varnishes.**—For this purpose urea-formaldehyde resins are made up in alcohol instead of water and it appears that alcoholic groupings are formed in the resin. These groupings increase their solubility in organic solvents and also increase their compatibility with alkyd resins with which they are often used. Reactions such as the following may occur:—



The type of alcohol used influences the properties of the resultant resins. Aliphatic alcohols of increasing chain-length increase the solubility of the resins in hydrocarbons, tung oil and alkyd resins. *n*-butyl alcohol, *n*-octyl and *sec*-octyl alcohols appear to be the most useful. Much of the alcohol is lost during the curing operation.

Urea-formaldehyde coatings by themselves have poor adhesive and mechanical properties. For this reason they are almost invariably mixed with alkyd resins in equal proportions. In this way a coating is formed which possesses the excellent adhesion and flexibility of the alkyd resins together with the hardness and quick-setting properties of the urea-formaldehyde resins. Since a cure at low temperatures can be obtained, delicate shades of colour may be retained during baking of the enamels.

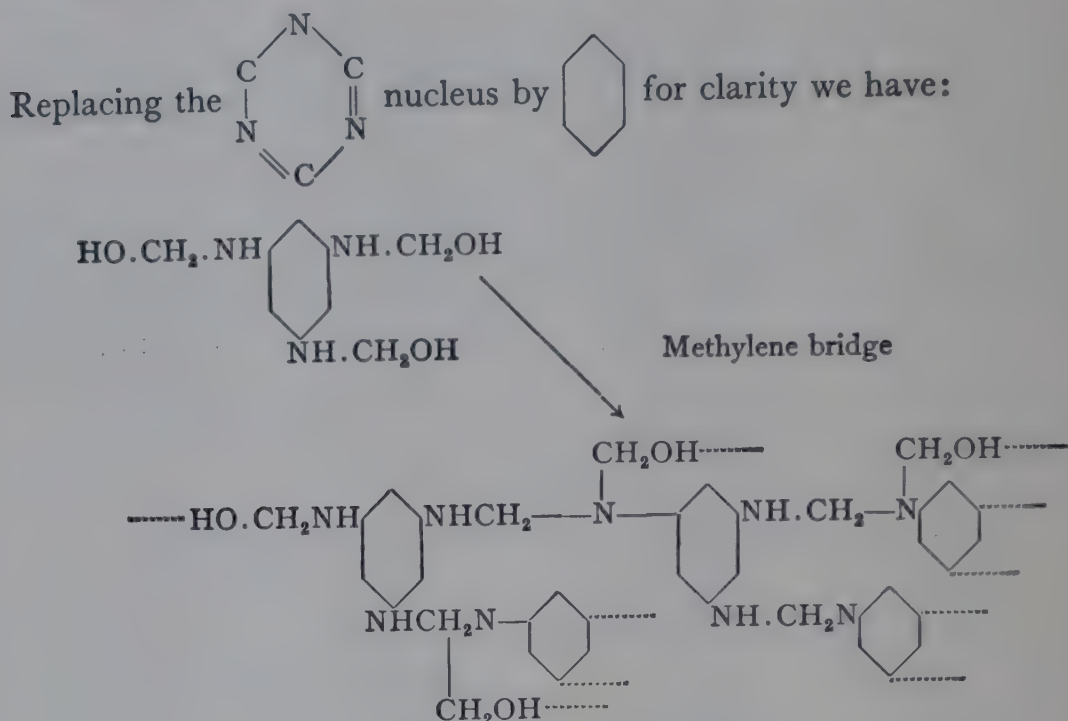
The enamels obtained are used on motor-car bodies, good bicycles, hospital equipment, and machinery in general.

**The Commercial Preparation of Melamine-Formaldehyde Resins.**—Most of the melamine-type resins available to-day are prepared by the direct condensation of melamine and formaldehyde. As in the case of dimethylol urea, these resins may be prepared so as to be water soluble, oil soluble, or insoluble. The first and last of these are really different stages of the same reaction. The oil-soluble type is a somewhat different material. The three materials available are determined by the ratio of the reactants, the catalyst, the temperature, and reaction time. The final product, as with urea-formaldehyde resins, is of a three-dimensional structure.

In practice the melamine resins are prepared as follows: Finely ground melamine (one molecular proportion) is mixed with 37 per cent. formalin adjusted to a pH of about 8.0 by means of caustic soda (five and a half molecular proportions). The resulting syrup after heating under reflux for about ten minutes is sprayed through a hot-air drier under a two-inch vacuum. The powdered white resin settles on the floor of the drier and is removed continuously.

The reactions involved during the curing of melamine-formaldehyde resins

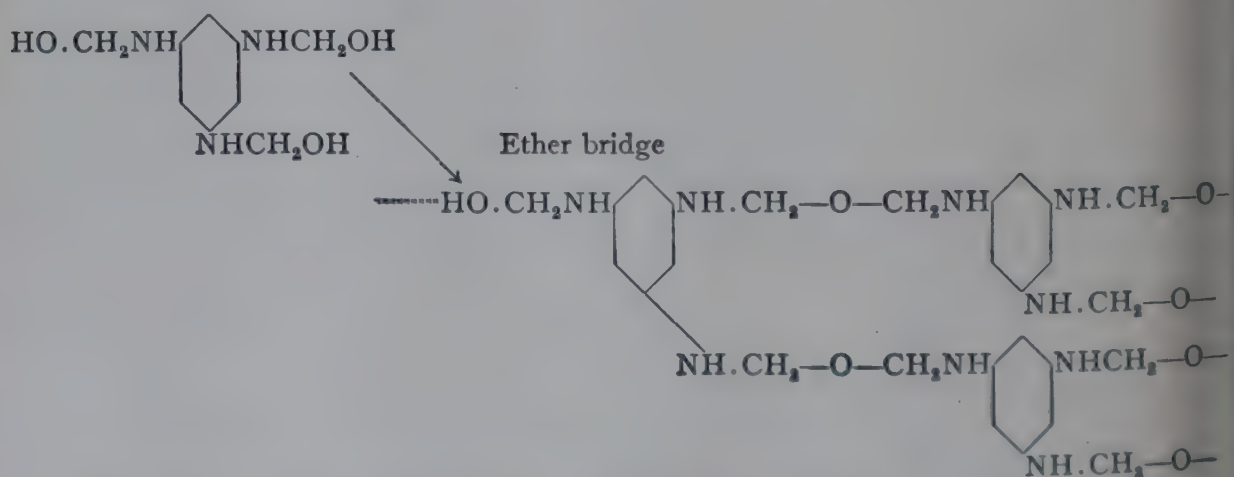
are thought to be more complicated than those taking place with urea-formaldehyde resins but a similar mechanism is thought to hold. Information is generally vague. There are two linkages which may exist between molecules of methylol melamines—the methylene bridge and the ether bridge, *e.g.*,



where ----- indicates reactive methylol groups.

It is seen from this that a three-dimensional structure may readily be built up

The ether linkage could be built up as follows: again simplifying the formula of methylol melamine,



Here again a three-dimensional structure may readily be built up.

**Applications of Melamine Resins.**—The unmodified resins are used in the textile and paper-coating industries. Water-soluble melamine-formaldehyde resins are modified by the addition of glycerol or related materials such as sugar. The products have the advantages of both phenol-formaldehyde and urea-formaldehyde resins—high softening-point, rapid setting-time, light colour, and good mechanical strength.  $\alpha$ -cellulose, pigments and other fillers may be added to modify the properties, or casting resins containing no fillers may be manufactured. Moulding powders are produced in a similar way to those from urea formaldehyde but those from melamine-formaldehyde are considerably harder, have improved heat resistance, lower water absorption, and greater resistance to acids and alkalis.

Moulded products such as domestic utensils are colourless, tasteless and



odourless, and will withstand hot water. Moulded electrical parts have very good electrical properties—high resistance to tracking, and a resistivity of  $10^{12} \Omega \text{ cm}$ .

Electrical uses include aircraft distributor parts, electric-iron handles and many other uses where heat and high voltage are present at the same time. Both phenolic and urea resins are inferior to melamine-formaldehyde resins as regards tracking resistance at high voltage.

Melamine-formaldehyde linings for food-containers are recommended, and melamine compositions are widely used as moulded food containers. Melamine compositions are more resistant to organic solvents, weak acids and alkalis than urea resins and are therefore most suitable for fruit juices containing acetic and citric acids.

Melamine-formaldehyde resins are frequently used for coatings, and for this purpose are modified with the common paint solvents and linseed oil. Alcohols are added during the condensation of melamine with formaldehyde as with the urea resins, giving an etherified resin which is more soluble in hydrocarbons. Sometimes melamine and formaldehyde are condensed in the presence of alkyd resins giving complex condensates which may be hardened by means of heat or catalysts or both to hard resistant films. The addition of 20 per cent. melamine resins to an alkyd resin reduces the stoving by half. Some of these films are heat resistant up to  $260^{\circ} \text{C}$ . and also very chemically resistant.

The absence of a  $-\text{CO}-$  group in the melamine resins accounts for their superior heat resistance in comparison with urea resins which are only heat-resistant up to  $180^{\circ} \text{C}$ .

Alkyd compounded melamine-formaldehyde resin solutions may be applied as coatings by dipping, spraying or brushing. When the solvents have evaporated, these compositions may be hardened by heating to  $150^{\circ} \text{C}$ . for only a few minutes. Temperature as low as  $80^{\circ} \text{C}$ . may be used for the hardening process. Urea resins require at least  $120^{\circ} \text{C}$ . These low temperatures enable steam-heated ovens to be used for the baking of melamine-resin films. White films of high gloss may also be obtained by the use of these low temperatures.

High-gloss melamine resin coatings are used for kitchen ware, *e.g.*, refrigerators, bathroom fixtures, electric irons, motor-car bodies, electric fire and stove parts where their heat resistance is an advantage.

**Laminated Materials from the Thermo-setting Resins.**—Practically any member of the family of plastics may be used to cause sheets of wood, paper or the like to adhere tenaciously when pressed together under the action of heat. The most familiar material of such a nature is plywood. The original material was bonded by means of glue, but nowadays plastics are used to an ever-increasing extent as the wood-bonding material.

One of the best known synthetic bonding materials is phenol-formaldehyde although in the past some of the natural resins such as shellac have been used.

For the production of laminated materials in general, the material to be plied-up, whether it be paper, fabric or thin wood, is first impregnated with a solution of the plastic, made up as described below, and the solvent allowed to evaporate. The dry sheets are then superimposed and subjected to heat and pressure in huge hydraulic presses where they are compacted to a dense uniform material which usually has a tensile and impact strength far above either the synthetic resin or the fabric vehicle.

The impregnating solution is usually a solution of a one-stage phenolic resin (*e.v.*) in alcohol. The fabric or paper is passed into such a solution and the excess solution removed by means of a doctor knife or squeeze rolls. From 20–80 per cent. synthetic resin content may be achieved by adjusting the doctor knife or squeeze rolls.

The impregnated paper or other material is then passed through a steam-heated chamber fitted with a solvent recovery plant.

When the impregnated material is dry, it is plied up and placed in a steam-heated hydraulic press. The laminate is then subjected to combined heat and



pressure which, in the case of a thermo-setting laminating material, causes it to harden, giving, for example, the familiar phenol-formaldehyde laminate. Other materials besides phenol formaldehyde may be used as laminating resins, even the thermoplastic resins such as polythene, in which case the press is cooled before removal of the laminate.

## CELLULOSE PLASTICS

### LITERATURE

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H. BARRON.—"Modern Plastics." Chapman & Hall. 1946.

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Several thermoplastics are based upon cellulose obtained from wood or cotton linters. Regenerated cellulose is described elsewhere in this book and is not generally recognised as a material of the plastics family. The following thermoplastics based on cellulose are now used in industry:—

Cellulose acetate and cellulose acetate butyrate, etc., ethyl cellulose and benzyl cellulose.

Cellulose acetate is undoubtedly the most important of the above materials.

### Manufacture of Cellulose Acetate

Briefly, it is manufactured by treating cotton linters with small quantities of mineral acids to increase the reactivity of the cellulose contained therein. After drying at about 50° C. the cotton linters are added to a mixture of twice their weight of cooled glacial acetic acid with their own weight of acetic anhydride.

A quantity of concentrated sulphuric acid equal to the weight of cotton linters is now added slowly, keeping the temperature below 10° C. The reaction mixture first becomes fluid and then begins to thicken up. After about five hours the linters have disappeared and acetylation is considered complete. Cellulose triacetate is formed. Water is then added slowly to react with any unchanged acetic anhydride. A dilute solution of acetic acid results.

Cellulose triacetate is not in great demand owing to its restricted solubility in common solvents. For this reason it is converted into the di- and monoacetate by a process of ripening. The ripening is generally stopped when the maximum quantity of the diacetate has been formed. The diacetate is obtained by careful dilution of the ripened solution which precipitates the product in the form of a finely divided white powder. This is centrifuged, washed and then stabilised by boiling with dilute mineral acid. After washing and drying, the product is ready. The product in greatest demand has an acetic content of 52–54 per cent.

### Properties of Cellulose Acetate

The properties depend largely upon the degree of acetylation, but we shall only describe here the best-known materials.

Cellulose acetate is extremely tough and possesses high impact strength. It is glass clear and transmits ultra-violet light very well.

It is unaffected by weak acids, oils, greases, and non-polar solvents such as petrol. It is hydrolysed by alkalis and therefore unsuitable for use in their presence. Unplasticised cellulose acetate has a softening-point ranging between 250° and 300° C. and soon begins to clear at such temperatures. For this reason the material is almost invariably plasticised by means of high boiling-point esters such as diethyl phthalate, methyl cellosolve phthalate, triacetin, triphenyl phosphate and diphenyl phthalate. A blend of plasticisers is always used to give the best results.



When we plasticise cellulose acetate we convert a hard, brittle, unworkable solid into a softer, pliable material capable of being manipulated at a much lower temperature. By carefully choosing the plasticiser the water resistance of cellulose acetate (never excellent) may be improved in addition to improving the toughness, hardness, flexibility, flame resistance, oil resistance, and light resistance. When the cellulose acetate is to be used for injection moulding, the flow characteristics must be regulated by carefully controlled plasticiser content.

### The Processing of Cellulose Acetate

The plasticisation of cellulose acetate is carried out in an internal mixer of the Werner-Pfleiderer type. A typical composition might be

Cellulose acetate	100 parts.
Dimethyl phthalate	20 parts.
Diethyl phthalate	20 parts.
Acetone	33 parts.
Benzene	33 parts.
Alcohol	33 parts.

This mixture is made at 40° C. until the mass is homogeneous. Much of the solvent passes off during mixing, which may require 3 hours. Solvent recovery plant is fitted which condenses most of the evaporating solvent. The dough from the Pfeiderer mixer is strained through a hydraulic strainer to remove foreign matter. The strained dough is then rolled on mills so that a thick band of material is formed round one roll. Further quantities of the solvents pass off into the hood over these mills, which are warmed to facilitate this operation. When the material has acquired a thicker consistency it is removed from the rolls as a slab about one inch thick. This slab is then treated according to the finished product required.

When sheets are to be made, the slab is cut into a suitable weight and placed in a large block mould with means of fixing the moulded block to the base of the mould. After several hours of heat and pressure the block is cooled under pressure for a similar time and sheets of various thicknesses sliced off the top. Traces of solvent are removed from these sheets by hanging them in a hot atmosphere. After surfacing between chromium plates they are ready for various applications such as windows (safety glass), dials, protractors, etc.

Cellulose acetate for extrusion is manufactured in a similar way to that described above except that smaller quantities of plasticiser are used, giving a stiffer product. Vast quantities of cellulose acetate are extruded as rod for constructional purposes where a coloured or transparent product may be required. Pigments are pre-mixed in a Werner-Pfleiderer-type mixer.

Cellulose acetate moulding compounds are manufactured in granular form by taking thin sheets from a mill and passing them through a Masson cutter which comprises a number of short knife-edges revolving against a cylinder also containing knife-edges. The action of a large number of powerful scissors in series is obtained. This moulding powder is used in huge quantities for the manufacture by injection moulding of numerous everyday articles such as babies' rattles, bottle caps, handles, imitation jewellery, and combs.

For those not conversant with the principles of injection moulding it may be mentioned briefly here, but is not a truly chemical subject. The moulding powder is placed in a hopper H (Fig. 239) feeding an electrically heated

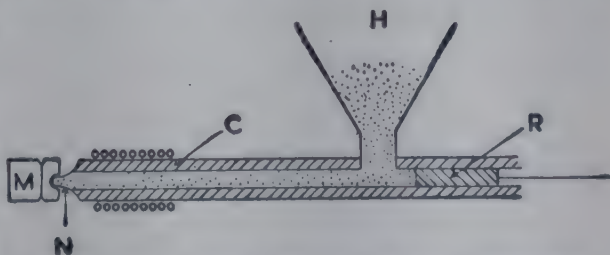


FIG. 239.—The Principle of an Injection Moulding Machine.

cylinder C through which passes a ram R. This ram pushes a given quantity of material into a mould M held against the nozzle N by a clamp. When R moves back again, the material in H falls into the empty space vacated by the ram, and the press is ready for another moulding.

Fillers are not generally used in cellulose-acetate moulding compositions as they spoil its toughness and other mechanical properties.

Cellulose acetate film is another large outlet for this material. Film is generally made from cellulose acetate containing a plasticiser. This is dissolved in acetone so that the finished dope has 40 per cent. plasticiser and 25 per cent. acetate. After filtering under pressure and standing to remove air bubbles, the dope is cast on to a moving endless gelatine-coated copper band totally enclosed in a glass cabinet. The dope is fed at constant level into a V-shaped trough with a slot at the bottom. The slot feeds a constant supply on to the travelling band and the temperature of the band is raised as each point travels farther from the slot. In this way the acetone is slowly evaporated from the film. Air from the chamber is passed through exhaust outlets to a solvent recovery plant. At the far end of the band the semi-dry film is stripped off, drying completed in a hot atmosphere, and the dried film wound up and later slit to the required size.

### Some of the Physical Properties of Cellulose-Acetate Unplasticised Film and Plasticised Sheet.

Property.	Unplasticised film.	Plasticised sheet.
Density . . . . .	1.4	1.3
Refractive index (sodium light) . . . . .	1.48	1.5 (approx.)
Tensile strength (dry) lb./sq. inch . . . . .	5000	3000-8000
Tensile strength (wet) lb./sq. inch . . . . .	4000	2000-6000
Elongation (dry) per cent. . . . .	7-10	up to 50
„ (wet) . . . . .	..	..
Dielectric strength v./mil. . . . .	1400	600-1000
„ constant 1 Kc./s. . . . .	6	4.5
Water absorption per cent. in 48 hours . . . . .	6	3 (approx.)

For further information concerning this well-established plastic the reader is referred to one of the books in the literature at the beginning of this section.

## THE ETHENOID PLASTICS

The group of plastics commonly grouped under this name comprise some of the most interesting and useful plastic materials yet discovered. In the space available for this section it will not be possible to deal with every member of this large family in detail. It is therefore proposed to mention as many as possible briefly and to enlarge upon one member in particular.

Radar during the 1939-45 War would have been impossible on the scale finally achieved without polythene (the generic term given to products formed on polymerising ethylene). It is proposed to treat this interesting plastic in fair detail.



## POLYTHENE

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## History

In 1930 one of the research departments of Imperial Chemical Industries embarked on a programme of fundamental research into the mechanism of chemical reactions at extremely high pressures. Pressures varied from 15,000 to 300,000 lb./sq. inch. No very startling discovery was made until ethylene became the subject of investigation. In 1933 it was found that when ethylene had been subjected to high pressures, a trace of white material remained in the reaction vessel after the pressure had been released and the cover removed. This was shown to be a polymer of ethylene. Polyethylenes or polythene, as the materials are called generically, have been shown to consist fundamentally of long chains of methylene groups thus:



$n$  may be 500 or more.

It was not until 1935 that enough polythene had been made for a systematic study of its properties to be conducted. By this date also the techniques for handling such enormous pressures had been considerably improved. Larger and more efficient equipment had been constructed. Work was not, however, completely without setbacks. Several violent explosions occurred in the reaction vessels, with considerable damage to equipment and laboratory. Undaunted by this unexpected behaviour, work continued in an effort to explain the explosive decomposition of ethylene. It was soon found that the purity of the ethylene used had a considerable influence on the tendency to explode.

By 1937 continuous running on a small pilot plant had been achieved, and later, in 1938, a larger improved pilot plant was in action.

The time was now ripe for an investigation into industrial uses for this new material, which was found to have a remarkable combination of properties: excellent electrical characteristics at high frequencies of the order of 100 mc./s. and upwards; great toughness and flexibility; lightness and a water resistance unparalleled except possibly by that of polyvinylidene chloride.

When contact was made with the electrical industry in 1938 the Telegraph Construction and Maintenance Co. were considerably interested by the resemblance between polythene and the gutta-percha based dielectric materials they have used for a hundred years for the insulation of submarine telegraph cables. An experimental length of submarine cable was made in 1938, and in 1939 a mile was made for the British Post Office, who saw the advantages of polythene over gutta-percha when electrical properties are considered.



Until 1939 ultra-high-frequency cables such as are used in television were predominantly air-spaced as no dielectric was in existence which would satisfy the electrical requirements and yet be sufficiently flexible. Polythene was found to be an admirable material for television transmitter and receiver cables.

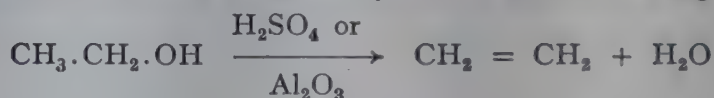
Thus we notice that although polythene was discovered during fundamental research with no industrial end in view it has fulfilled a need as yet unfulfilled by any other material with such excellent results.

The demand for polythene by the Telegraph Construction and Maintenance Co. at the beginning of the war for the insulation of both submarine and radar cables showed that a full-scale manufacturing plant for polythene was a necessity. From this period the manufacturing capacity of Imperial Chemical Industries has increased manifold in order to satisfy the demand for polythene. During the war many cables were made at very short notice for urgent military requirements. Many were laid across the Channel for "D-day." At the end of hostilities those responsible for their manufacture received a letter from Mr Winston Churchill in appreciation of the fact that they had enabled him to keep in continuous contact with the front line.

The romance of polythene is one that could be told at greater length than this, but it is now necessary to turn to more practical aspects of this material.

### The Manufacture of Polythene

The raw material used for the manufacture of polythene is ethyl alcohol. This is heated in the presence of a dehydrating agent such as alumina or sulphuric acid, which converts it into ethylene in the following way:—



Ethylene may also be obtained from coke-oven gases or from the cracking of petroleum. The manufacture of polythene from petroleum ethylene is planned in the near future. It should be remembered, however, that the purity of the ethylene for the high-pressure reaction is most important.

Whilst it is known that ethylene may be polymerised by the application of heat and pressure using such catalysts as aluminium chloride, boron trifluoride, zinc chloride and oxygen, the industrial manufacture employs one part of oxygen in several million of ethylene. Temperatures up to 300° C. are used in conjunction with pressures up to 30,000 lb. per square inch. The conditions of temperature and pressure determine the molecular weight of the polymer produced. High pressures produce tough, high molecular-weight polymers, while low pressures produce oils, greases, or waxes. The polymerisation of ethylene is thought to follow the generally accepted principle of chain initiation and growth. Free radicles are formed which give rise to a chain propagation reaction. The commercial products are divided into "Grades." The Grade is determined as a melt viscosity. It is the number of grams of polythene which will flow through an orifice 2.08 mm. in diameter under a pressure of 16.1 lb./sq. inch in 10 minutes at 190° C. Commercial grades are 2, 7, 20, 200, although grades from 200,000 to 2,000,000 may be obtained in addition to these of the order of 0.1. The latter are almost unprocessable so great is their toughness at all temperatures.

Although a sample of polythene may have a grade number of 20, this does not imply that the molecular weight of the product is uniform. The average chain length of the molecules may be 1000 carbon atoms, but some molecules may be present with chain lengths of 600 and some with chain lengths of, say, 1200. It is generally thought that the low molecular-weight impurities in polythene tend to yield an inferior product. Efforts are continually being made to restrict the "band spread" of molecular weight in any given grade. Polythene made in the United States appears to possess a considerably greater molecular-weight spread than that made in Britain. For example, a sample of American polythene



was found to have a grade of 1.0 and could be extruded readily at 140° C. on a cable-covering machine. British polythene of this grade must be extruded well above 200° C. The explanation of this may be that the American polythene was plasticised by low molecular-weight polymers.

### Physical and Chemical Properties of Polythene

Polythene is a white, translucent material which can just be marked by means of the finger-nail. It is often said to resemble paraffin wax, but, in fact, the only resemblances are the empirical formula  $(CH_2)_n$ , where there is a vast difference between the values of  $n$  in the two cases and the fact that both have the greasy touch common to most of the softer organic materials.

The polymers of ethylene are substantially saturated, linear molecules, chemically related to the low molecular-weight paraffins, although work with infra-red spectroscopy has shown the presence of  $CH_3$  and other side chains in addition to some  $-CO-$  groups, especially when oxidation has taken place.

There is a substantial quantity of crystalline material in polythene, the proportion of which may be varied by its heat-treatment history. This will be described later under processing. The axis dimensions of the polythene crystal have been found to be

$$\begin{aligned}a_0 &= 7.4 \text{ \AA}^\circ \\b_0 &= 4.93 \text{ \AA}^\circ \\c_0 &= 2.53 \text{ \AA}^\circ\end{aligned}$$

$c_0$  is the identity period along the chain.

When a thin section of polythene is viewed through a polarising microscope, the familiar dark crosses are seen. This indicates that the crystals are arranged in a spherulitic manner. Like most other crystalline polymers, polythene may be cold-drawn. When this occurs, the spherulites are orientated along one axis—in the direction of drawing. An X-ray diffraction photograph of cold-drawn polythene shows the well-known fibre diagram spots.

Although the empirical formula of polythene is written in a similar way to the lower paraffins, the mechanical properties are vastly superior. This is explained by the greatly increased chain length of polythene, which provides many more van der Waal's forces per molecule. These are generally accepted to be the forces causing materials to "hold together."

An interesting feature of solid polythenes of different molecular weight is that they all possess a crystal melting-point of 110°–115° C. When polythene is gradually raised in temperature, no substantial change in crystallinity occurs below 60° C., above which temperature the proportion of crystalline material gradually diminishes until the material is completely amorphous and glass clear at 115° C.

The density of polythene at 20° C. is 0.92 gm./c.c. At 115° C. it is 0.80 gm./c.c. There is a sharp fall in the density of polythene at the melting-point.

The following table shows the relationship between "grade," molecular weight and viscosity of a number of polythenes:—

Grade.	Molecular weight (average).	Viscosity in poises (approximate).	
		190° C.	120° C.
2	20,000	30,000	1,000
7	18,000	9,000	..
20	16,500	3,000	10,000
200	22,000	..	100,000



It will be noticed that a relatively small alteration in molecular weight causes considerable variation in grade (*i.e.*, ease of extrusion under constant pressure).

Although the crystal melting-point of all grades of polythene is  $110^{\circ}$ – $115^{\circ}$  C., the deformation point under considerable load increases with diminishing grade number. Most grades of polythene are suitable for use up to  $80^{\circ}$  C. providing considerable loads are not applied. Grade 2 may be used for most purposes up to  $100^{\circ}$  C.

The behaviour of polythene under mechanical stress is governed by two important facts:

(a) Recovery of polythene from deformation up to a certain limit is practically complete. The harder the grades, the more complete is this recovery.

(b) The lower the temperature the more brittle polythene becomes, the higher the temperature the more plastic it becomes. The brittle temperature of polythene lies between  $-25^{\circ}$  C. and  $-100^{\circ}$  C., depending upon the grade. Grade 2 is more resistant to embrittlement at low temperature than Grade 200.

Polythene can be cold-drawn after the yield-point is reached. The tensile strength varies between 1270 lb./sq. inch for Grade 200 to 2000 lb./sq. inch for Grade 2.

The elongation at break varies from 100 per cent. with Grade 200 to 400 per cent. with Grade 2.

Young's modulus varies from 23,000 lb./sq. inch for Grade 200 to 26,000 for Grade 2.

The outstanding resistance of polythene to cold flow or creep under both tension and compression is worthy of mention. The hard grades (low number) are useful as sealing rings for glands up to a temperature of  $100^{\circ}$  C. The extent of deformation is approximately proportional to the logarithm of the time of application of the load in the case of tension for loads up to 40 per cent. of the yield stress.

Under compression the deformation is even smaller than under tension. Recovery from compressive deformations of 60 per cent. at  $20^{\circ}$  C. is practically complete. The higher molecular-weight polythenes recover more completely than those of lower molecular weight, especially at high temperatures ( $>90^{\circ}$  C.).

The impact strength of polythene Grade 20 is 12.5 ft./lb. on a 150-lb. Avery machine (0.5 sq.-inch bar).

The toughness (measured by the work done in stretching a cube of material to its breaking-point and recorded in kg./cm.) is shown to be greater than raw rubber, gutta-percha, cellulose acetate or polystyrene. The latter has a toughness only one-seventieth that of polythene.

The surface hardness of polythene is low compared with many plastics. Polythene can be marked by means of the finger-nail. The Brinell hardness is approximately 2, rising to 2.5 for the hardest grades. Grade does not greatly influence the surface hardness. The latter seems to be affected more by the mechanical treatment received by the polythene sample prior to testing, *e.g.*, whether the surface is oriented by lapping or whether the sample has been stretched. The above values of hardness were obtained on a specimen 1.5 mm. thick, using a 2-mm.-diameter ball and a load of 3 kg. The temperature was  $20^{\circ}$  C. and the reading was taken 30 seconds after application of the load.

### The Electrical Properties of Polythene

The 1939–45 War boosted the importance of the electrical properties of polythene. Several other plastics (polystyrene, polyisobutylene) possess electrical properties nearly as good as those of polythene, but they do not possess these in combination with remarkable mechanical properties as does polythene.



The main electrical characteristics of polythene are as follows:—

Power factor at 16 mc./s.: 0.00015–0.00025 (there is only a slight rise with frequency).

Dielectric constant: 2.3.

Volume resistivity:  $10^{17}$ – $10^{20}$  ohm./cm.

Dielectric strength: 1000 volts per mil.

As the electrical properties of polythene are little altered by changes in frequency, the material may be used at all frequencies with little distortion due to loss at certain frequencies.

The applications of polythene on account of its excellent electrical properties will be surveyed under "Applications of Polythene" below.

### The Chemical Properties of Polythene

The chemically saturated nature of polythene accounts for its phenomenal water resistance and chemical inertness. The water resistance is second only to saran (polyvinylidene chloride). Polythene is practically unaffected chemically by all reagents at room temperature. Many organic solvents, however, especially the polar ones, cause considerable embrittlement and loss of toughness simply by the process of absorption without chemical action.

Oxidising acids such as nitric and strong oxidising agents such as chlorine begin to attack polythene at temperatures above 50° C. Above 58° C. polythene becomes soluble in aliphatic hydrocarbons, chlorinated aliphatic hydrocarbons, aromatic hydrocarbons and other solvents containing no oxygen. The high molecular-weight polymers are less soluble above 58° C. than the low molecular-weight polymers. They are also less affected by the embrittling action of polar solvents.

**Oxidation.**—When polythene is heated in air to above 80° C. or thereabouts very slow oxidation occurs, resulting in cross-linking of the straight chain molecules, toughening of the polymer, a severe decrease in the grade number after a time, and a rise in the power factor. This form of oxidation takes place in the presence of limited amounts of oxygen. When polythene is severely oxidised at very high temperatures actual chain cission takes place, with a rise in power factor as before, but with a severe increase in grade number.

As the temperature of oxidation rises, the rate of oxidation increases. Below 130° C. the rate of oxidation is sufficiently slow to enable normal processing (mixing, extrusion, or moulding) to be carried out provided care is taken to keep the periods at which the material is exposed to this temperature to the minimum.

When polythene is to be used as a high-frequency dielectric it is important to restrict the rise in power factor caused by contact with the air to the minimum. Most of the antioxidants used in rubber technology, when incorporated into polythene, retard oxidation. The staining tendency of most of these antioxidants is a disadvantage, as they spoil the inherently clean appearance of polythene by turning it brown or orange.

Although it is not a perfect antioxidant at the highest temperatures, nonoxol D.C.P. (di-*o*-cresylol propane) is commonly used in polythene. It is suitable up to 170° C. for long periods and only changes the colour of polythene slightly. "Agerite White" is a better material for the highest temperatures but unfortunately stains polythene badly.

### Water, Aqueous Solutions, Acid and Alkali Resistance

The water absorption of polythene after prolonged immersion is normally less than 0.05 per cent. by weight with negligible dimensional changes. The permeability of polythene film to water vapour expressed in the units gm./sq. cm./hour/mm.



of mercury pressure difference is less than  $4.5 \times 10^{-9}$  at  $40^\circ \text{C}$ . and 93 per cent. R.H.

Polythene may be used in contact with all common acids and alkalis in any strength at room temperature with the following exceptions:—

Nitric acid (conc.)—not above  $50^\circ \text{C}$ .

Chlorosulphonic acid—not at all.

Acetic and low aliphatic acids—not at all unless in dilute aqueous solution.

Embrittlement takes place, not chemical action.

Other strong oxidising acids—not above  $50^\circ \text{C}$ .

Polythene provides an excellent container for hydrofluoric acid of all strengths (see under Applications).

Polythene is resistant to salt water indefinitely, hence its use in vast quantities for submarine cable manufacture (see below).

### Resistance to Other Materials

Polythene is attacked by halogens slowly, and rapidly at higher temperatures. The use of polythene with halogens is therefore not recommended. Embrittlement and change of colour follows. In the presence of ultra-violet light, halogens attack polythene vigorously with the formation of halogenated polythenes which are of use as adhesives.

Polythene, although not chemically attacked by any solvent at room temperature, absorbs considerable quantities of many of these, more in the case of those which are solvents at higher temperatures, but it is found that polar non-solvents of polythene possess greater embrittling action at room temperature. Examples of the latter are methanol, acetone, and methyl methacrylate.

Many other chemicals are absorbed by polythene without chemical action, but with deleterious action on mechanical or electrical properties or both. Examples are sulphur (electrical), camphor (mechanical and electrical), and *p*-dichlorobenzene (mechanical and electrical), plasticisers for P.V.C. such as tricresyl phosphate, dioctylphthalate and other phthalates (mechanical and electrical). The use of these materials, or materials containing them, in contact with polythene should not be practised (*e.g.*, in cable manufacture).

### Compounding and Applications of Polythene

Polythene is not normally mixed with other materials, except where they confer advantages which outweigh their disadvantages. All fillers in any but pigmentary proportions spoil the mechanical and electrical properties. Anti-oxidants are used in proportions of the order of 0.1–0.2 per cent. with valuable advantages as mentioned above.

Carbon black of fine particle size is added as in rubber technology to confer resistance to the photo-ageing effect of ultra-violet light with its consequent degradation of mechanical properties. Two per cent. is normally used.

Polyisobutylene, a synthetic rubber, is used in large quantities in admixture with polythene for, although slight loss in tensile strength and hardness follows, the advantages of using this rubbery polymer, which has excellent electrical properties, are manifold. A few advantages are:

- (a) Sensitivity of polythene to processing temperature is reduced.
- (b) Resistance to embrittlement by polar solvents is increased markedly.
- (c) Ease of incorporation of fillers is increased and their effect on the mechanical properties of polythene is reduced.
- (d) Low temperature flexibility is increased.

For the compounding of polythene, normal rubber-mixing machinery may be used (*e.g.*, mills with scrapers to remove the molten, sticky, plastic material). Werner-Pfleiderer-type mixers are also excellent, provided the blades are carefully



designed. The blades should not hold large quantities of material which forms "dead spots" in the machine, resulting in poor mixing.

Cold-feed extruders are in use by some manufacturers, in which case blending machinery is not normally used. The raw materials are obtained in granulated form for direct feeding to the extruders.

Some of the most important uses of polythene are as follows:—

- (1) Submarine cables.
- (2) High-frequency and other cables.
- (3) Electrical mouldings.
- (4) Piping and containers for chemicals and edible liquids.
- (5) Tank linings (in sheet and powdered form).
- (6) Film for moisture-resistant wrappings and condenser dielectrics.
- (7) Paper, textile, and metal-foil coating for moisture proofing.
- (8) General electrical constructional work by machining from polythene in the massive state.
- (9) Miscellaneous.

**1. Submarine cables.**—Polythene, in modified form to provide specific characteristics (Telcothene, Reg. Trade Mark), has partly taken the place of gutta-percha in the insulation of submarine telegraph cables. Telcothene possesses the following advantages over gutta-percha for this purpose.

- (a) Greatly superior electrical characteristics resulting in faster working of telegraph services.
- (b) Multi-channel telephone services with up to 100 conversations may now be run.
- (c) It is a cheaper dielectric.
- (d) It does not age with time.
- (e) It has a water resistance better than gutta-percha or even pure polythene.

Telcothene is extruded on to copper conductors to various diameters up to nearly 2 inches on specially designed machines with extra precautions to avoid the difficulties encountered in extruding large sections. These large sections are then armoured for protection when laid on the sea-bed.

**2. High-frequency and other cables.**—Pure polythene is extruded by means of simple extruders of the cold-feed or hot-feed type, with particular care to

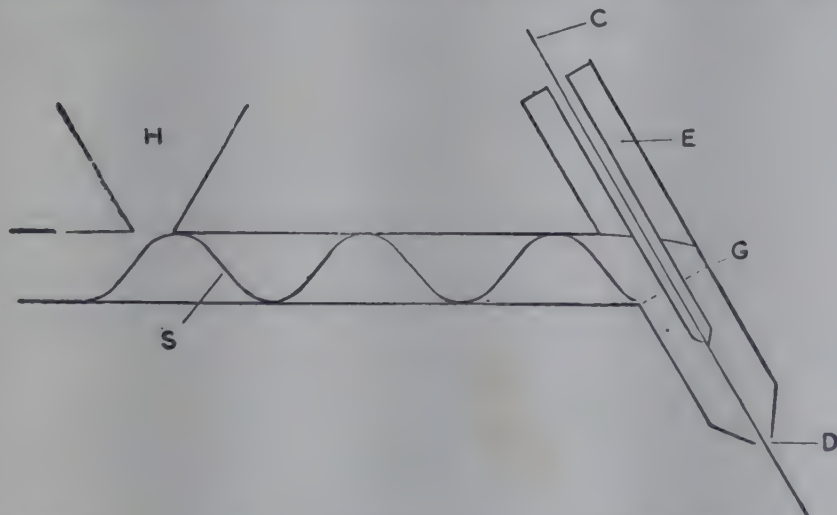


FIG. 240.—A Diagrammatic View of a Cold Feed Extruder.

avoid rise in power factor due to oxidation at processing temperatures. Fig. 240 shows the general principle of a cold-feed extruder. Granulated polythene is fed into the hopper H and falls on to the screw S, where it is heated by steam, but mostly by friction, and enters the extrusion head E, passes through the gauze G, and then through a die D, with the copper conductor wire C.



Hot-feed machines are also used with great success, but their design is too complex to be indicated here.

Where extreme heat resistance is required, grade 2 and lower numbers are essential. It is then that a cold-feed extruder can be used to best advantage, *i.e.*, when the viscosity of the melted material is sufficiently high to grip the screw and provide ample extrusion pressure.

In all extrusions the polythene should be cooled slowly in near boiling water in order to reduce strain formation and contraction voids.

**3. Electrical mouldings.**—Polythene may be injection, extrusion, and compression moulded with ease. The high contraction and sharp melting-point of polythene necessitates fast filling of the mould with continuous follow-up pressure until the moulding has set.

**4. Piping for chemicals and edible liquids.**—Polythene may be extruded from a tubing die to give a tube of almost any size. The tube must be spray-cooled and held in shape by means of compressed air. After extrusion it is supported on a conveyor belt until completely set.

**5. Tank linings.**—Polythene or the polythene-polyisobutylene mixtures may be calendered into sheet and welded with polythene welding rod and a hot nitrogen jet into tank linings for the storage of corrosive chemicals.

Recently a new technique has been developed whereby polythene is reduced to a powder by a patented process and the article to be coated is heated and dipped under this powder, thereby picking up sufficient powder to form a film on reheating. These films are very acid resistant.

The process is used for coating electroplating jigs.

Polythene powder may, of course, be sprayed on to tanks by the usual well-known techniques such as those devised by the Schori Company.

**6. Film.**—Polythene may be extruded and drawn into thin film from  $1\frac{1}{2}$  mils. upwards in thickness. This film may be used for moisture-resistant wrappings and for condenser dielectrics. Film may also be made by extruding thin-walled tubing and expanding this while hot. After cooling, it is slit down one side and opened up into film, or is used in tubular form for working up into polythene bags for storing pastes, etc.

**7. Paper, textiles and metal-foil coating.**—These materials are readily coated with polythene by means of the doctor-knife technique, in which the material to be coated passes between a rubber roller and a vertical blade slightly raised from the roller. Temperatures of  $150^{\circ}\text{C}$ . upwards are required, and the softer (higher grade number) polythenes are best used for this purpose.

Calendering may be used as a means of coating materials with polythene. As high temperatures cannot be used on account of the danger of adhesion to the calender rolls, it is essential to dry and heat the material to be coated prior to coating.

When metal foil is to be coated, the coated foil should be heated for about a minute at  $280^{\circ}\text{C}$ . to improve the adhesion to the foil. This toughens the coating by slight oxidation as well as bringing about slight chemical bonding between the metal oxide on the metal surface and oxidised polythene.

**8. General electrical constructional work with polythene.**—Polythene may be cast into blocks of almost any size by careful attention to cooling rate, otherwise contraction voids are produced. These blocks may be machined with ease into any required shape.

**9. Miscellaneous uses of polythene.**—Briefly these are: anti-spray balls in chrome-plating baths (acid resistance); discs for air-spaced high-frequency cables; catheters for medical work (complete inertness and freedom from toxicity); as a base for radio-active materials in cancer research; bottle wads (chemical resistance); bottle manufacture; other laboratory ware such as beakers, funnels, tubes, dishes, etc. (chemical resistance).



## POLYVINYL CHLORIDE

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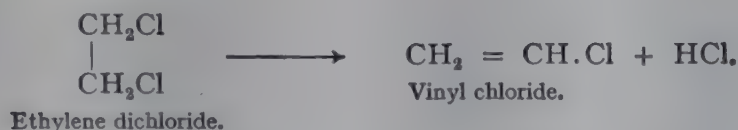
## Manufacture

This thermoplastic is prepared by polymerising a gas—vinyl chloride. The latter has a boiling-point of  $-14^{\circ}\text{C}$ . at atmospheric pressure. Vinyl chloride is made by two methods:

(a) The catalytic combination of acetylene and hydrogen chloride in the presence of a mercury salt



(b) The removal of hydrogen chloride from ethylene dichloride either by heating in vapour form or by treating in the liquid form with a strong alkali such as aqueous caustic soda.



Vinyl chloride is polymerised both in solution, pure or in emulsion, with the aid of an oxidising catalyst. As in most polymers, the length of the polymer chain largely decides the properties of the product, both from the point of view of solubility and mechanical properties. Conditions of polymerisation are carefully chosen to give a long molecule for most purposes, free from short ones.

The finished polymer is a fine white powder with a faint but characteristic odour which may be due to slight decomposition. Polyvinyl chloride is one of the least stable polymers.

## Properties and Plasticisation

Polyvinyl chloride possesses a remarkable resistance to most inorganic acids, alkalis and organic solvents with the following few exceptions. It is dissolved by ketones, tetrahydrofurane and similar solvents, and solvents such as trichloroethylene and toluene have slight swelling effects.

The polymer may be moulded and extruded between  $170^{\circ}\text{C}$ . and  $200^{\circ}\text{C}$ ., but long heating without adequate stabilisation causes considerable decomposition. Even after stabilisation (see below) the unplasticised polymer is very liable to decompose. Decomposition is catalysed by some metals, in particular zinc, iron, and copper. Nevertheless a large proportion of polyvinyl chloride is still processed in iron machinery.

The best stabiliser for polyvinyl chloride is basic lead carbonate. Many others are used, however, for special purposes such as for producing a transparent product.

As stated above, pure polyvinyl chloride has a high softening-point and readily decomposes at this temperature. For this reason, for most purposes considerable quantities of high boiling-point esters are used as plasticisers in order to obtain a more rubbery and more easily processed product. Unplasticised polyvinyl chloride is manufactured in the form of sheet, rod, and tube for the construction of chemically resistant plant. Plasticised polyvinyl chloride has much wider applications. It resembles natural rubber in texture when moderately plasticised, and many of its applications are as substitutes for rubber, *e.g.*, shower curtains, bathroom curtains, cable coverings, tubing (garden hose), flooring, shoe soles, and raincoats.

Polyvinyl chloride may be plasticised by mixing with between  $\frac{1}{3}$  to  $\frac{1}{2}$  its weight of a high boiling ester such as dioctyl phthalate or tricresyl phosphate. The latter are by far the best plasticisers to use, but dibutyl phthalate (too volatile) and most other esters are plasticisers for P.V.C. Extenders such as Cerechlor (chlorinated paraffin) are very useful and are compatible up to certain proportions. They cheapen the mix, besides imparting improved electrical properties in the case of Cerechlor. Up to 8 per cent. (calc. on polymer) of basic lead carbonate or other stabiliser is incorporated during plasticisation, in addition to pigments which may be inorganic or organic lakes. The mixing is normally carried out on a mill at  $160^{\circ}$ – $170^{\circ}$  C., but a Werner-Pfleiderer mixer heated to  $180^{\circ}$  C. is satisfactory.

The physical properties of plasticised P.V.C. are governed to a large extent by the nature and quantity of plasticiser employed. Compositions containing as little as 5 per cent. plasticiser are rigid, whilst those containing 50 per cent. resemble soft rubber and may be flexible down to  $-60^{\circ}$  C.

The electrical resistivity of plasticised P.V.C. varies from about  $10^{15}$   $\Omega$  cm. when the quantity of plasticiser is low, to  $10^{11}$   $\Omega$  cm. when it is large. These values also depend largely on the electrical characteristics of the plasticiser. The power factor and dielectric constant are both inferior to those of polythene and polystyrene (pure hydrocarbons), and consequently polyvinyl chloride has extremely limited high-frequency uses. It was, however, used in enormous quantities for the outer protective sheath of radar cables during the 1939–45 War. As a sheath, of course, the P.V.C. is not in the high-frequency field.

### The Theory of Plasticisation

There is not full agreement on the finer detail of plasticisation theory. Present-day theories will be given here.

When a plasticiser is mixed with a solid thermoplastic resin such as polyvinyl chloride, the plasticiser first enters microscopic cracks and fissures in the resin after wetting the surface. All liquids will be more or less absorbed by a polymer whether they are good plasticisers or not. Later, if the plasticiser is a suitable one, it enters the spaces between the molecules of the polymer. In the unplasticised polymer the polymer molecules are held together by van der Waal's forces between them. As the plasticiser proceeds in its action, the polymer-polymer contacts are broken because of the entry of plasticiser molecules which "sandwich" themselves between the polymer molecules.

The structure of the polymer thus becomes a more open one built up from polymer-plasticiser-polymer "bricks and mortar." The polymer chains are lubricated by means of the plasticiser. The greater the quantity of the latter, the greater the softening afforded. A more flexible product, more liable to deformation by rise in temperature, is produced.



Some of the desirable properties of a plasticiser are as follows:—

- Compatibility with the polymer.
- Stability at plasticising temperatures.
- Low vapour pressure.
- Freedom from marked odour.

There are many other desirable properties, but these are dictated by the particular application of the plasticised polymer.

As a guide to the mode of use of a plasticiser, take the case of polyvinyl chloride. This is a hard, brittle resin with a softening-point in the region of  $200^{\circ}\text{C}$ ., at which temperature considerable decomposition takes place in the presence of iron and other metals. When, however, 100 parts of polyvinyl chloride are mixed with 60 parts of a plasticiser such as dioctyl phthalate, together with up to 8 parts of a heat stabiliser such as basic lead carbonate, and heated to  $180^{\circ}\text{C}$ . in an internal mixer such as a Werner-Pfleiderer or Banbury, or on mills, a complete transformation of the resin-plasticiser mixture takes place from a dry paste to a sticky viscous liquid at  $180^{\circ}\text{C}$ ., cooling to a rubbery material at  $130^{\circ}\text{C}$ . Further cooling gives a hard, rubbery solid at room temperature.

### Uses of Polyvinyl Chloride

We have already mentioned the application of polyvinyl chloride to the sheathing of high-frequency cables.

Screw extruders of both cold and hot feed are used for this purpose, although the cold-feed extruders appear to give better results with this comparatively unstable plastic. For a description of both these types see under **Polythene**. This and the application to "house wiring" and other low-voltage cables is still probably the most important use of P.V.C. Other uses which are gaining prominence are those connected with the leather-cloth industry, where P.V.C. is calendered on to cloth for the manufacture of upholstery. A variation of this technique is to spread a mixture of polymer and plasticiser with stabiliser and pigments on to cloth and to plasticise *in situ* under infra-red lamps.

A minor but interesting application of P.V.C. is in the manufacture of hollow dolls and other soft objects by a casting technique. An unplasticised thin paste is made from polymer, stabiliser, and pigment, with more than the usual quantity of plasticiser. This is poured into a mould, which is then heated to form a semi-plasticised skin on its inner surface. Excess of paste is poured out and the plasticisation of the skin continued to completion. On cooling, the object may be stripped from the mould. Flexible sink traps have been made in this way. These may be squeezed when they become blocked!

We have only described polyvinyl chloride above, but it should be mentioned that a co-polymer of vinyl chloride and acetate is used in a similar way to the above compounds.

## POLYSTYRENE

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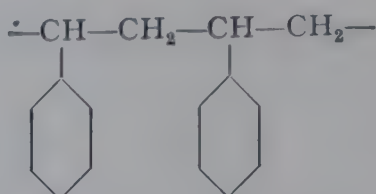
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### Manufacture of Polystyrene

When styrene (vinyl benzene,  $\text{C}_6\text{H}_5\cdot\text{CH}=\text{CH}_2$ ) is heated or exposed to ultra-violet light in the presence of a small quantity of a catalyst of the peroxide type, such as benzoyl peroxide, it polymerises to form polystyrene.



Polymerisation is usually carried out in bulk, although emulsion polymerisation may be used.

Depending upon the chain length, a brittle or tough polymer is produced. Long chain molecules are tough; short chain ones are brittle. Considerable research has been conducted towards the production of a polymer which shall contain no short chain molecules, for the presence of these in a polymer substantially of high molecular weight leads to crazing of the surface and tendency towards brittleness.

### Properties of Polystyrene

Commercial polystyrene is a colourless solid, rather brittle in comparison with polythene or even **Perspex** (see below). It is normally marketed in the form of sheets or in the form of a moulding powder (Lustron). Like polythene, it is a polymer with extremely good high-frequency electrical properties. It is resistant to strong acids, alkalis, alcohols, and petroleum solvents (aliphatic), but is dissolved by aromatic solvents. The water transmission of polystyrene is surprisingly high compared with its low water-absorption of less than 0.08 per cent. after 24 hours. (Compare polythene, 0.05 per cent.)

Polystyrene is thermoplastic, softening from about  $100^\circ\text{C}$ . (depending upon the molecular weight) and becoming free flowing after  $160^\circ\text{C}$ . At  $180^\circ\text{C}$ . to  $200^\circ\text{C}$ . it can be injection moulded, using pressures of 1,000 lb. per sq. inch. These mouldings are used in large quantities by the electrical industry. Unless care is taken to use polystyrene absolutely free from low molecular-weight polymer, hair-like cracks develop in mouldings. Methods of removing low molecular-weight polymers, such as by heating in a vacuum for a few hours, have been adopted. Also the use of chlorinated diphenyl in the monomer prior to polymerisation has been said to assist in preventing this troublesome phenomenon.

### Uses of Polystyrene

In addition to its high-frequency electrical uses on account of its excellent power factor (0.0001 to 0.0002), polystyrene is used for lens manufacture on account of its transparency. Thin film is not particularly brittle and is used for high-frequency cable manufacture by lapping. Polystyrene may be machined for electrical constructional purposes. Large quantities of polystyrene are used for the manufacture of disc-spacers for high-frequency cables.



## POLYACRYLIC PLASTICS

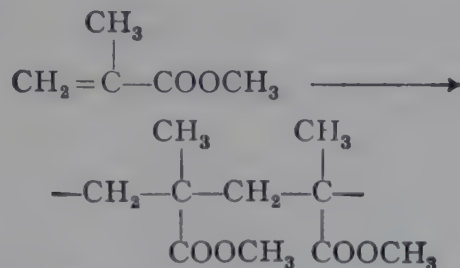
## LITERATURE

I.C.I. Brit. Pat. 405, 699.

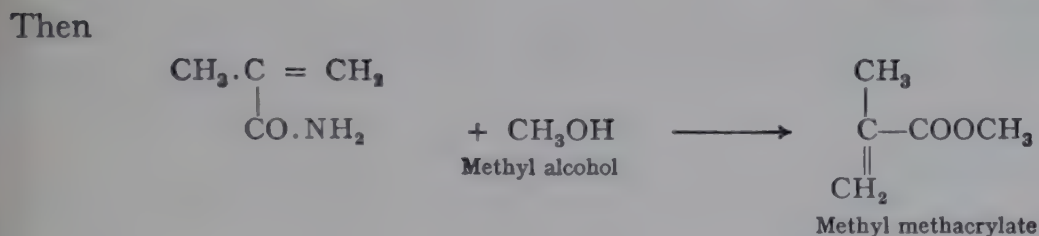
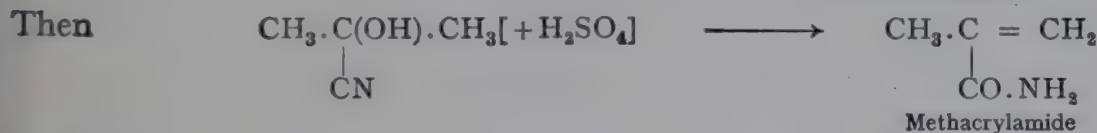
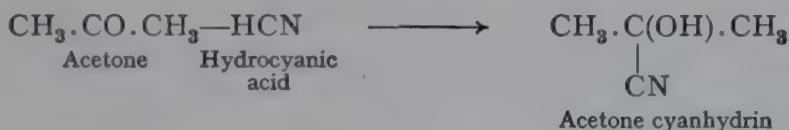
*Modern Plastics*, vol. 22, No. 2, Oct. 1944, p. 97.

These comprise polymethylmethacrylate, polyethylmethacrylate and polybutylmethacrylate. Only the first, which is manufactured by I.C.I. under the trade name Perspex, will be described.

Polymethylmethacrylate is produced by the polymerisation of methylmethacrylate,



Methylmethacrylate is obtained commercially by treating acetone (from molasses) with hydrogen cyanide, methyl alcohol, and concentrated sulphuric acid.



Methyl methacrylate is a transparent liquid with a boiling-point of 100° C. It is usually polymerised by means of a peroxide catalyst by the mass process. In the manufacture of Perspex sheet, for instance, the monomer, with catalyst added, is poured into glass moulds placed in an oven at a carefully controlled temperature.

## Applications of Polymethyl Methacrylate

Although Perspex is thermoplastic, it never actually melts. Its softening range begins at about 100° C., and the material is generally manipulated between this temperature and just below 200° C. At 200° C. decomposition begins. Sheets are formed into domes for aircraft, etc., at temperatures between 120° C. and 150° C., either by blowing by compressed air or by pulling over formers.

There are two varieties of Perspex sheet on the market. One of them contains a small quantity of plasticiser such as dibutyl phthalate. This is added to the monomer before polymerisation. Plasticisation gives a sheet more easily manipulated during forming, but means that the softening-point of the finished article will be lower. Articles such as lenses are moulded from unplasticised Perspex of a special grade.

Perspex moulding granules are prepared unpigmented or pigmented and injection moulded into a variety of shapes. Some examples are denture plates and teeth. Actually, these are often hand-moulded in a plaster cast from a dough made up of polymethyl methacrylate and the monomer. This mixture is then polymerised in boiling water.

For moulding purposes, the polymer chain is usually kept shorter than for the preparation of sheet. This is in order to give a polymer with good flow properties.

The polymer is prepared in the form of emulsion and solution for textile treating and varnishes or coating materials.

## THE POLYAMIDE PLASTICS

### LITERATURE

CAROTHERS AND HILL.—“Artificial Fibres from Synthetic Linear Condensation Superpolymers,” *J.A.C.S.*, 1932, vol. 54, p. 1579.

HOFF.—“Nylon as a Textile Fibre,” *Ind. Eng. Chem.*, 1940, vol. 32, p. 1560.

BOLTON.—“Development of Nylon,” *Ind. Eng. Chem.*, 1942, vol. 34, p. 53.

ASTBURY.—“Types of Man-made Fibres,” *Endeavour*, 1944, vol. 3, p. 98.

LOASBY.—“Nylon Yarn,” *Chem. and Ind.*, 1944, vol. 32, p. 282.

### The Nylons

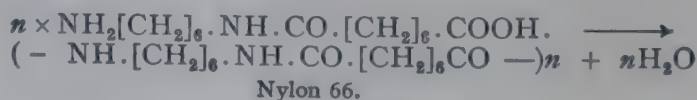
Nylon is the best-known member of this group of plastics. It is the generic name for a group of polyamide plastics, but has become well known as the name for the reaction product between adipic acid and hexamethylene diamine —“Nylon 66.”

### Manufacture of Nylons

All these plastics possess one characteristic in common, namely, that they are manufactured from bifunctional molecules. By this we mean that the molecules reacting each have two groups taking part in the reaction. The chemistry of the manufacture of nylon will demonstrate this. The reaction that takes place is as follows:—



Polymerisation then takes place as follows:—



The  $[\text{CH}_2]$  chain in both the acidic and basic ingredients may be varied at will within certain limits, but the details of these other nylons cannot be described here. For further details the reader is referred to the literature at the beginning of this section.

### Properties of Nylon

Nylon 66 is an opaque white crystalline solid with a density of 1.14 gm./c.c. melting sharply at 264° C. into a treacle-like liquid.

Cold-drawn nylon filaments possess a tensile strength of 58,000 lb./sq. inch, falling to 43,000 lb./sq. inch with 100 per cent. R.H. Thus nylon filaments compare favourably with natural fibres such as silk. The elongation at break of nylon is 30 per cent.



The abrasion resistance of nylon is very good. It is for this reason that nylon has been chosen for many of its modern applications (see below).

Nylon may be subjected to 100° C. for several days without appreciable change in physical properties and may be subjected to 150°–180° C. for short periods.

Nylon ages in sunlight in a similar way to natural fibres.

The electrical properties of dry nylon are fair, but in the presence of a high humidity they deteriorate somewhat as shown in the following table:—

R.H.	Temp.	Vol. Resistivity.	S.I.C.	Power Factor.
18%	22° C.	$4 \times 10^{14}$ ohm. cm.	4	0.05
100%	22° C.	$5 \times 10^9$ ohm. cm.	20	0.11

The breakdown voltage is 1300 v./mil. on 0.009-inch film.

Nylon is slightly hygroscopic, and this is one of its most important characteristics in view of its application in the textile industry. The water absorption is 7 per cent. at 25° C. and 100 per cent. R.H.

Nylon is not resistant to strong acids. It is, however, very resistant to strong alkalis.

Nylon is most resistant to all common organic solvents except formic acid, phenol, metacresol, cresylic acid and xylene, and similar materials.

The resistance of nylon to mould growth is excellent, and there is no reason to believe that it is toxic to human life.

### Applications of Nylon

Based upon the above properties, the following uses of nylon have grown:

**1. Brushes.**—One of the first large industrial uses of nylon was in the manufacture of tooth brushes, the bristles of which remain stiff and straight for many years longer than those from natural resources. Many other brushes are now made from nylon monofilaments.

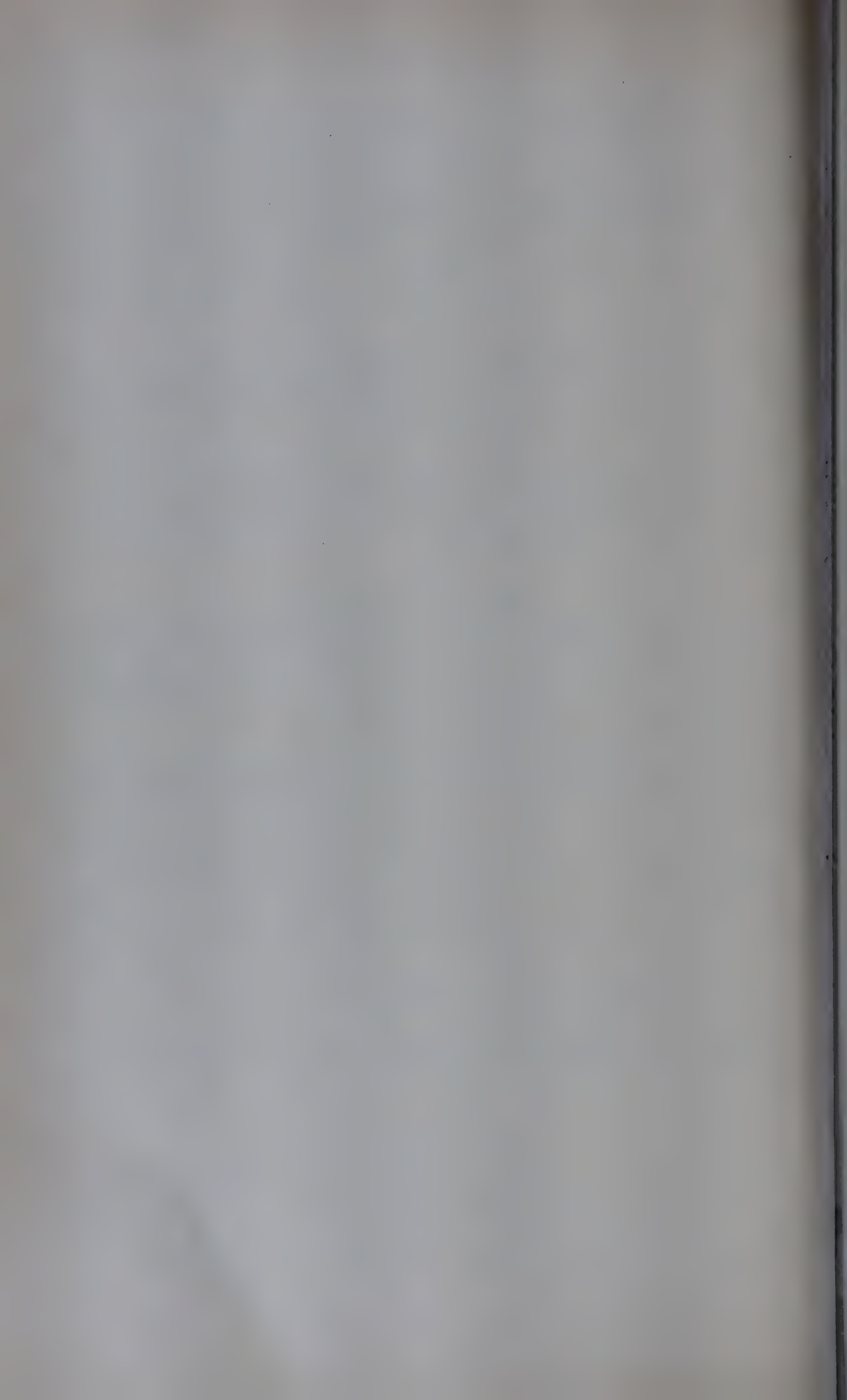
**2. Racquet strings and fishing lines.**—These are now on the market as they are harder wearing than the catgut and linen materials formerly used. They do not fray.

**3. Surgical sutures.**—Nylon sterile sutures are of even diameter, consistent strength and practically non-absorbent, with a very smooth surface rendering withdrawal smooth and easy. They also possess a very clean appearance.

**4. Ropes.**—Owing to its phenomenal strength and resistance to abrasion, nylon found an important use in the 1939–45 War for glider tow-lines and parachutes, both cords and fabric.

**5. Cable sheaths.**—Nylon is rapidly becoming established as an abrasion-resistant sheathing material for wire ropes and electric cables.

**6. Artificial silk stockings.**—Last, but by no means least, the spinning of nylon into thin threads and their manufacture into stockings is well known to all.





SECTION XXIII

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The Industry of Photographic Chemicals





# THE INDUSTRY OF PHOTOGRAPHIC CHEMICALS

Originally written by G. MARTIN, Ph.D., D.Sc.  
Revised by E. I. COOKE, M.A.(Cantab.), B.Sc., A.R.I.C.

## LITERATURE

- BENTLEY AND SOUTHWORTH.—“Photographic Chemicals and Chemistry.” 1949.  
CRABTREE AND MATTHEWS.—“Photographic Chemicals and Solutions.” 1939.  
ILFORD.—“Manual of Photography.” Greenwood, London, 1947.  
MEES.—“Photography.” G. Bell & Sons Ltd.

THE manufacture of photographic chemicals is a modern industry of great and rapidly growing importance.

We can only give in this place an account of the more important substances especially manufactured for photographic purposes. Chemicals which are widely employed in other industries—such as sodium thiosulphate, salts of gold, silver, platinum, etc.—cannot be discussed here, since an account of these technically important salts will be given in the second volume of this work.

**Statistics.**—The United States imported in 1910—Moving picture films, 12,830,000 lin. ft., of value \$771,000. Photographic plates and other films, value \$416,000. Photographic paper, value \$762,000.

The American export of photographic goods is shown by the following figures :—

1906	1907	1908	1909	1910
\$256,000	\$1,090,000	\$2,840,000	\$4,185,000	\$4,765,000

The United Kingdom in 1913 *exported* £1,065,700 of photographic materials. The *import* in 1913 was £2,372,000. The value of the photographic materials (plates, paper, and films), produced in Great Britain in 1907 was £909,000.

Although exact statistics are at present unobtainable, the magnitude of the industry of photographic chemicals may be gauged by the fact that one factory in England alone orders its potassium bromide in 30-ton lots, and that one company is the largest user of silver except a Government mint! The production of the biggest English photographic paper factories runs to *miles*, and of plates to *acres* per day. Many thousands of workers are employed in the industry.

For modern statistics see Appendix III.

## CHEMICALS EMPLOYED IN THE MANUFACTURE OF PHOTOGRAPHIC PLATES AND FILMS

**Plates.**—The ordinary plate is a specially selected best quality thin glass sheet, covered with an extremely light-sensitive layer of silver bromide particles suspended in gelatine. The glass, cleaned by automatic machinery by brushing and spraying with soda and water, is coated with a substratum consisting of a weak solution of gelatine containing chrome alum, which causes the emulsion to adhere to the glass and prevents “frilling,” then dried by hot air and coated with the sensitive emulsion by a special machine, dried in a special room, cut to the proper size by machinery, examined for defects by red light, and packed.

The **Emulsion** is made by adding a 20 per cent. solution of silver nitrate to a potassium bromide solution containing gelatine. A more concentrated solution will produce “pepper,” which reveals itself as a countless number of fine black particles of silver which are more or less evenly distributed throughout the emulsion when coated. Negative emulsions usually have a small percentage of KI added to the gelatine, while diapositive and “gaslight” paper emulsions consist chiefly of silver chloride with a very little bromide. After mixing, the emulsion is “ripened” by keeping at a high temperature for some time, or by digesting at a lower temperature with ammonia, then



it is cooled by ice until it sets to a jelly, forced by hydraulic pressure through small holes in a metal plate, and the threads thus produced washed free from the  $\text{KNO}_3$  (formed thus:  $\text{AgNO}_3 + \text{KBr} = \text{KNO}_3 + \text{AgBr}$ ). When the emulsion has been prepared by the ammonium nitrate method it is very important to free the shreds from ammonia. According to Dr A. B. Hitchin, the nature of metals used for the forcing plate are of the utmost importance, any metals other than silver or pure nickel producing a fog in the emulsion. The system of forcing the emulsion by pressure through the plate is now being replaced by the use of a large machine on the principle of a meat chopper, the whole being made of pure cast nickel. The "fastness" of the plate depends upon the size of the grains of  $\text{AgBr}$ —the larger the grain the faster the plate.

**Collodion Wool** is simply nitrated cotton, the manufacture of which is described on pp. 207, 624.

**Collodion** is its solution in a mixture of alcohol and ether, usually containing 5 per cent. of wool.

The solvent rapidly evaporates in the air, leaving a skin. It is used in the manufacture of silver bromide collodion emulsions and for making light filters.

**Celluloid** is used for the manufacture of camera and cine-films, also as a protective covering for pictures, being for the latter purpose coated with an adhesive. For the manufacture of celluloid see p. 208.

**Cellite, or Cellulose Acetate**, is used for the same purposes as celluloid; although dearer it has the great advantage over celluloid that it is practically non-inflammable. For its manufacture see pp. 210, 216, and under Plastics, p. 640.

**Gelatine** is largely used for the manufacture of plates, and for making light-sensitive emulsions of silver halides. For the manufacture and properties of gelatine see p. 595.

The ordinary dry plate is covered with an extremely light-sensitive layer of silver bromide particles suspended in gelatine. The gelatine on the plate may be hardened after development by soaking in a solution of formalin or of alum.

**Albumen and Casein** used in the manufacture of photographic papers. For manufacture and properties of albumen see p. 597, and for casein, p. 79.

## DYES USED IN THE PREPARATION OF PHOTOGRAPHIC PLATES AND FILMS

Silver halides are most sensitive to blue and violet light rays, and least sensitive to red rays. Various dyes are used to render silver halides treated with them more sensitive to red, yellow, and green rays, so that the true colours are better reproduced in the resulting picture than would otherwise be possible.

The dye may be added to the sensitive emulsion either before pouring it on to the plate, or it is applied to the dry plate after manufacture by immersing it in a dilute solution of the dye and then allowing the plate to dry. For example, in the case of cyanin dyes a solution containing 1 part dye : 1,000 water is used, and 2-4 c.c. of this solution is added to 100 c.c. of a mixture of 40 c.c. alcohol + 60 c.c. water. The plates are bathed in the solution for two to three minutes and then dried at  $18^\circ$ – $24^\circ$  for ten minutes—the whole operation being carried out in the dark. Plates which have been thus rendered almost equally sensitive to all the rays of the spectrum are termed "**panchromatic**," while those which are especially sensitised for green and yellow—very important for landscape pictures—are the so-called "**orthochromatic**" plates.

When ortho plates are bathed in pinacyanol, the plate is hypersensitised, and exposure necessary reduced to one-fourth its original amount. The plate is



immersed for ten minutes in the bath, which consists of 1 milligram of pinacyanol in 1 c.c. alcohol + 1,000 c.c.  $H_2O$  + 2 drops  $NH_3$ .

The following are the most important dyes used as sensitisers:—

**The Phthaleins.**—Of these **erythrosin** and **eosin** are widely used for rendering silver bromide sensitive to yellow and green rays, and consequently for the manufacture of “**Ortho-chromatic**” plates.

**Monobromfluorescein** is used as a green sensitiser for silver bromide.

Among the **Rosaniline dyes** we may mention that **Ethyl violet** and **Formyl violet** are used as red sensitisers of silver bromide collodion emulsions. **Akridin dyes** are used to some extent as sensitisers for green and blue.

Among the **Azo dyes** used as sensitisers we may mention: **Benzonitrol brown** (By), **Dianil black R** (M., L., & Br.), **Glycin red** (By), **Pluto black** (By), **Wool black 4B** (Agfa). The dyes known as **Alizarin blue bisulphite** and **Nigrosin D** are used to some extent as red sensitisers.

### Quinoline Dyes

Are now very important sensitisers (see p. 479). Among them we must mention:—

#### a. Cyanines

**Cyanin** (Lepidinquinolineamylcyaniniiodide), a blue dye, quite useless for textile purposes on account of its fugitiveness, but used as a sensitiser for silver bromide plates where a panchromatic effect is desired. It renders silver bromide sensitive to red, orange, and yellow rays, with a minimum of sensitiveness between E and F. Its defects are a tendency to fog and speck the plate, accompanied with a diminution in its light-sensitiveness. As a red sensitiser it has been displaced by isocyanines, but it is still used for wet plates and for special kinds of work. Vogel uses a mixture of this dye with quinoline red under the name “**Azalin**” for sensitising dry plates for green and yellow.

**Ethylcyanin** (Lepidinquinolinethylcyaninbromide), being more soluble than cyanin, has been proposed as a substitute.

**Dicyanin** (prepared by action of  $KOH$  + atmospheric O on  $\alpha$ - $\gamma$ -Dimethylquinolinium salts) sensitises silver bromide gelatine plates up to the red line  $\alpha$ , with a strong minimal effect between E and F. Used as a red sensitiser for scientific work, but the prepared plates are not very sensitive.

#### b. Isocyanines

Of these dyes the most important are:—

**Ethyl red**, or quinaldinquinolinethylcyanin iodide, which forms green crystals soluble in water and alcohol, with a violet-red colour. In dilute solution (1 : 50,000) it sensitises silver bromide gelatine plates almost uniformly from the red (C) to the violet, with only a small minimum in the green. It does not sensitise far into the red.

Preparations of isocyanines and similar dyes, which are sensitive further in the red, have been put on the market by Meister, Lucius, & Brünig in Höchst-a.-M., under the names **Orthochrom T** (which is  $p$ -Toluquinaldin- $p$ -Toluquinolinethylcyaninbromide), **Pinachrom** (which is  $p$ -Ethoxyquinaldin- $p$ -methoxyquinolineethylcyaninebromide), and **Pinacyanol** (which is obtained by treating quinaldinium salts with formaldehyde, followed by alkali), the latter sensitising in the red up to the B line. **Pinaverdol**, produced by the same firm, is a green sensitiser for silver bromide collodion emulsions, and consists of  $p$ -Toluquinaldinquinoliniummethylcyaninbromide.

*Fr. Bayer* in Elberfeld also places several sensitisers on the market. Among these we may mention:—

“**Perikol**,” prepared by treating with alcoholic  $KOH$  the addition product



obtained from Toluquinaldin and the ethyl ester of Toluene sulphonic acid, sensitises plates to a maximum between  $\lambda = 590$  and  $\lambda = 560 \mu\mu$ . "Isokol" is a similar preparation. "Homokol" is a mixture of quinoline red with an isocyanine dye.

Some of Fr. Bayer's more interesting patents are German Patents, 158,078, 170,048, and 170,049, where the process of manufacture of a number of sensitising dyes are described by acting with alkalis on the addition products of dialkylsulphates with quinaldin and its homologues. The new colouring matters are stated not to fog or fleck plates.

### Dyes used for Colour Filters and Similar Purposes

Coloured screens or filters are an absolute necessity in many photographic processes, and a very large number of coal-tar colours are used for the manufacture of these colour filters, which may consist of collodion, gelatine, or aqueous fluids coloured with special dyes which only allow special wave lengths to pass, or which greatly diminish the intensity of the actinic rays.

The screens most widely used consist of glass plates covered with gelatine coloured with a suitable dye.

For developing ordinary dry plates in the dark room the filters used consist of red dyes, and for bromide, yellow dyes. For very fast plates both yellow and red filters are used. For panchromatic and colour-screen plates a faint green light is used.

**Auramine O** is very suitable, as it absorbs blue and violet, allowing red, green, and yellow rays to pass.

**Tartrazin** and **Fast Red D** (M., L., & Br.) are good red filters, so also is **Chrysosulphite** (Lumière), which is a mixture of magnesium picrate and sodium sulphite.

**Coxin** is also a very suitable red filter.

The dyes used for colouring gelatine must be water soluble and free from other adjuncts such as dextrin, Glauber's salt, etc. etc., otherwise the gelatine will not dry clear. The following dyes (among others) are used for colouring the gelatine :—

**Auramine**, **Brilliant green**, **Crystal violet**, **Fuchsin**, **Methylene blue**, **Phenosafranin**, **Rhodamin** (these also can be used for colouring collodion), also **Acid green**, **Congo red**, **Naphthol green**, **Naphthalene green**, **Filter yellow**, **Rapid Filter red**, **Rapid Filter yellow** (Meister, Lucius, & Brüning), **Patent blue**, **Tartrazin**.

### LIGHT FILTERS

The following light filters are recommended by *Meister, Lucius, & Brüning*, the filters produced being toned for orthochromatic and panchromatic plates :—

#### Light Filters for the Three-Colour Process

**Red Filter.**—2.5 g. filter red I. are dissolved in 100 c.c. warm water. 100 c.c. of 8 per cent. gelatine solution are mixed with 4 c.c. of the colour solution and the whole filtered, and 7 c.c. of the gelatine used for every 100 c.c.

**Blue Filter.**—4 g. crystal violet are dissolved in 100 c.c. warm water and 5-6 drops of acetic acid are added; then 6 c.c. of coloured solution are added to 100 c.c. of 8 per cent. gelatine solution, and the whole is filtered.

**Green Filter.**—2.5 g. tartrazine + 6 g. patent blue + 4 g. naphthol green dissolved in 400 c.c. water; 5 c.c. of colour solution are then added to 100 c.c. of 8 per cent. gelatine solution and the whole filtered.

Time of exposure with orthochromatic plates is blue : green : red :: 1 : 3 : 6.



## Light Filters for the Additive Three-Colour Prints

**Red Filter.**—4 g. tartrazine + 7.5 g. filter red II. in 150 c.c. water. Add 7-8 c.c. of this solution to 100 c.c. of 8 per cent. gelatine solution and filter.

**Blue Filter.**—3 g. crystal violet + 1 g. methylene blue (free from  $\text{ZnCl}_2$ ) + 100 c.c. warm water + 6 drops acetic acid. Add 7-8 c.c. of this coloured solution to 100 c.c. 8 per cent. gelatine solution and filter.

**Green Filter.**—6 g. tartrazine + 1 g. patent blue + 2 g. naphthol green + 180 c.c. water. 8-9 c.c. of coloured solution is used for 100 c.c. of 8 per cent. gelatine solution.

Times of exposure for orthochromatic plates are blue : green : red = 1 : 5 : 8; for panchromatic plates 1 : 4 : 3.

To make the dry filters 7 c.c. of the coloured gelatines made as above described are poured over every 100 sq. cm. of plate surface and allowed to set; then two coloured plates are taken together and fixed with Canada balsam.

In the three-colour photographic process such dyes as **Aurophenin** or **Naphthol yellow S**, **Erythrosin**, **Diamine pure blue** or **Fast bluish green** are used to colour the partial pictures.

## MODERN COLOUR PHOTOGRAPHY

The essential principles of colour photography have been known for nearly a century. The first colour plates were marketed about forty years ago. Considerable progress has been made in recent years, however, with transparencies which faithfully reproduce the colours of the original subjects. To-day it is possible for the amateur photographer to print photographs directly on to paper.

The possibility of colour photography was demonstrated by Clark Maxwell in 1861 when he took black-and-white photographs through different coloured filters (red, green, and blue), and then placed the positives in three lanterns. The light from these three lanterns was then passed through the three coloured filters through which the original photographs were taken. The result was projected on to a screen so that the three images were coincident. In this way a coloured picture was obtained. This principle has been used by many workers since Maxwell's time, but the need was for a colour photograph which could be held in the hand and which did not require a lantern for its observation.

The earliest successful process for colour photography was invented soon after 1900 by the Lumière Company in France, using an idea originally put forward by Hauron in 1869. The perfected process was called the Autochrome process and utilised little grains of starch dyed red, green, and blue, thoroughly mixed, scattered over the surface of the plate, and squashed into flat discs. The interstices were filled with carbon black and the whole surface varnished. The photosensitive emulsion was then coated on to the varnish. In this screen plate process, as in Clark Maxwell's method of triple projection, the colour photograph is formed by the admixture of coloured light of the three primary hues—red, green, and blue. Natural colours, however, are formed by the absorption of some of the components of white light impinging on the object emitting the colour.

Thus there are two distinct methods by which we may make coloured pictures from triple negatives: the additive method in which the colours are added in projection, and the subtractive method in which the colours are produced by the superposition of prints. The latter method is used in the production of illustrations in books.

Schinzel in 1905 proposed that coloured images should be obtained by placing red, green, and blue dyes in three layers, the actual colour of the dyes being developed by the reducing action of the silver image. The chief difficulty in this and later variations of this method was that the dyes tended to migrate into the adjacent layers.

In 1930 a number of new sensitising dyes were discovered and it was possible



to select those which did not migrate into the adjacent layers. After this progress was rapid and the Kodachrome process was placed on the market in 1935. The Kodachrome film was coated with three light-sensitive emulsions, the red next to the base, next the green, next a yellow filter layer which prevented the blue light from reaching the green and red-sensitive layers and, lastly, the unsensitised emulsion which recorded the blue and violet light. None of these layers contain dye-forming material. The latter is introduced during the processing of the exposed film. Originally it was necessary to process three times, introducing the dyes in turn, but improvements have been made so that the film can now be processed in one operation.

The modern Kodachrome process (1948) works as follows: After exposure the film is first developed with ordinary developer which develops the silver negative in the three layers. After washing the film is exposed to red light through the back. This renders developable the bottom layer of the three which was not previously exposed and therefore not developed in the first development. The film now passes into a developer, containing both a colour developer and a coupler, which will produce a blue-green positive in the bottom layer, because the developed blue-green image is produced from the silver bromide not exposed at the beginning and thus not developed in the first developer. It is reversed compared with the original negative exposed in the bottom layer.

The film is now exposed to blue light from the top and a yellow positive developed in the top layer. Finally the unexposed silver bromide in the middle layer is developed by means of a coupler-forming magenta dye, and the whole of the silver that has been formed in the various processes removed by means of a bleaching bath.

In order to obviate the rather tedious development process described above for the Kodachrome process, the Kodacolor process was introduced about 1940. In this process three types of coupler are dispersed in the three layers dissolved in minute globules of organic solvents dispersed in the gelatin emulsions. Thus, after development, the red-sensitive bottom layer gives a blue-green image, the green-sensitive middle layer gives a magenta image, and the blue-sensitive top layer gives a yellow image. The film is developed after exposure with a colour-forming developer which becomes oxidised during its action and then unites with the couplers to form dyes. The silver is removed by means of a bleaching bath. The resulting negative is in reverse—the whites are black, the reds are blue-green, the blues are yellow, and the greens are magenta. This negative is then printed on paper of the same type as that from which the negative was originally made. This gives a positive with the colours complementary to those of the negative, *i.e.*, the correct colours of the subject of the photograph. This seems to be the most popular type of colour film in use at the present moment.

Another variation of the above process is that marketed under the name Ektachrome. The film contains the usual three layers, each containing the appropriate coupler dissolved in the minute oil globules. The film is first developed with a "black-and-white" developer to obtain a negative. This is then re-exposed to white light and redeveloped with a colour developer.

The chemical nature of some of the materials used in colour photography is given in the following patents and references to the literature:—

*Trinuclear Cyanine Dyes for Sensitising Photographic Emulsions.* A. W. Anish, Assr. to Gen. Anil. and Film Corp. (U.S.P. 2,432,060, 2.12.47).

*Dye-coating Composition for Colour Photography.*—R. M. Haff, Assr. to Gen. Anil. and Film Corp. (U.S.P. 2,433,811, 30.12.47).

*Diaz-type Layers containing Thiourea Derivatives of Hydroxybenzene.*—W. H. von Glahn and L. N. Stanley, Assrs. to Gen. Anil. and Film Corp. (U.S.P. 2,432,549, 16.12.47).

*Diazo-type Prints with Hydroxypyridone Couplers.*—J. F. Morgan, Assr. to Gen. Anil. and Film Corp. (U.S.P. 2,431,190, 18.11.47).

*Naphthol Sulphonamide Colour Developers.*—A. B. Jennings, Assr. to E. I. Du Pont de Nemours & Co. (U.S.P. 2,435,629, 10.2.48).



*Acyl-substituted Reactive Methylene Couplers.*—A. Weissberger, C. J. Kibler, and H. D. Porter, Assrs. to Eastman Kodak Co. (U.S.P. 2,436,130, 17.2.48). These are claimed to give non-diffusing properties by the substitution of the reactive methylene group by an acyl group.

*Tripack Film with Emulsion Layers adjacent to each other.*—J. C. Crawford (U.S.P. 2,435,957, 17.2.48).

*Sensitised Photographic Emulsions.*—Kodak Ltd. and E. B. Knott (B.P. 593,056, 18.5.44). Describes the use of naphthiazoles.

*Colour Photography.*—J. D. Kendall, H. G. Suggate, and Ilford Ltd. (B.P. 593,065, 8.6.45). A coloured image is formed in an emulsion layer, carrying an image in a reducible silver salt, by developing in the presence of strong alkali at 20° C. with aryl hydrazones of the type *p*-ethoxy-phenyl-hydrazone, *p*-methylthiophenyl- and 2-naphthyl-hydrazone.

*Cyanine Dyes and Materials containing them.*—Eastman Kodak Co. and G. H. Keyes (B.P. 599,712, 6.10.45). Discusses the preparation of *meso*-substituted trimethincyanine dyes.

*Cyanine Dye Intermediates and Dyes.*—E. B. Middleton and G. A. Dawson, Assrs. to E. I. Du Pont de Nemours & Co. (U.S.P. 2,424,483, 22.7.47). Methincyanine dyes and trimethincyanine dyes are described.

*Dichromate Bleach Bath.*—R. O. Egerton, Assr. to Eastman Kodak Co. (U.S.P. 2,428,208, 30.9.47). A bleach which will not remove appreciable amounts of dye from a coupled dye and the alkyl-naphthalenesulphonic acids (wetting agents) are discussed.

*Colour Couplers for Photographic Colour Development.*—A. Bavley, Assr. to Gen. Anil. and Film Corp. (B.P. 599,719, 3.11.45).

*Manufacture of Aminopyrazolones and their Use as Colour Couplers.*—A. Weissberger and H. D. Porter (B.P. 599,919, 11.12.44).

*Heterocyclic Colour Couplers.*—A. Bavley, Assr. to Gen. Anil. and Film Corp. (U.S.P. 2,418,748, 8.4.47). Discusses increased activity and coupling speed obtained by using 5- or 6-membered *n*-heterocyclic quaternary compounds in which the N carried a di-, tri-, or tetra-methylene chain linked to the adjacent C.

*Trinuclear Cyanine Sensitising Dyes.*—A. W. Anish, Assr. to Gen. Anil. and Film Corp. (U.S.P. 2,427,177, 9.9.47). A new class of trinuclear cyanine sensitising dye is claimed.

*Manufacture of Intermediates and Photographic Sensitising Dyes made therefrom.*—Kodak Ltd. and E. B. Knott, F. M. Hamer, and R. J. Rathbone (B.P. 594,558-9, 1.3.45).

*Formation of Coloured Photographic Images by Colour Development.*—Dufay-Chromex Ltd. and B. Gluck and M. Planka (B.P. 593,938, 20.6.45). Discusses the use of NN-dialkyl-*p*-phenylenediamine hydrochloride in the presence of a colour former such as an alkyl or aryl or mixed aryl-alkyl ester of 1 : 2—OH.C<sub>10</sub>H<sub>6</sub>.CO<sub>2</sub>H.

*New Process of Colour Photography.*—J. Rzymkowski (*Fotographie*, 1948, No. 3, 63-64).

*Open Chain Active Methylene Colour Couplers.*—A. Weissberger and H. D. Porter, Assrs to Eastman Kodak Co. (U.S.P. 2,439,352, 6.4.48).

*Synthetic Linear Polyamide Dye Intermediates and Process of Colour Photography employing same.*—E. I. Du Pont de Nemours & Co. (B.P. 598,367, 29.3.45).

*Non-diffusing Phenolic Colour Couplers.*—A. Bavley, Assr. to Gen. Anil. and Film Corp. (U.S.P. 2,418,747, 8.4.47).

*Advances in the Chemistry of Dyes used as Sensitisers for Photographic Silver-halide Emulsions.*—P. Kainrath (*Angew. Chem.*, 1948, 60, A, 36-42).

*Modern Colour Photography.*—C. E. K. Mees (*Endeavour*, 7, No. 28, 131-140).

The treatment given above to the subject of colour photography is, of necessity, very brief, but it is hoped it will give the reader food for thought and further reading in literature devoted entirely to the subject.

## FLASHLIGHTS

Powdered magnesium was introduced as a flashlight in 1887. Since then many other flashlights have been introduced—usually by mixing the magnesium with an oxygen-rich substance. Many of these preparations are very explosive, and must not be blown into a flame. We may notice the following recipes:—

1. 2 parts Mg powder + 3 parts powdered potassium permanganate.
2. 15 parts Mg powder + 30 parts KClO<sub>3</sub> + 5 parts antimony sulphide, finely powdered and mixed dry. Explosive, so must not use a mortar.
3. Smokeless flashlight mixtures giving an intense light consist of magnesium or aluminium powder + nitrates of rare earths (thorium, zirconium). See German Patent, 158,215; see also English Patent, 27,267 (1904), where rare



earths are added to Mg or Al flashlights. Fr. Bayer & Co. (German Patent, 136,313) place a number of excellent flashlights on the market; they appear to consist of Mg + manganese peroxide, to which are added bodies like  $\text{Sr}(\text{NO}_3)_2$ , which yield a coloured flame. See also English Patent, 27,466 (1904). Such mixtures are termed ortho- or panchromatic flashlights, since they give out orange rays in addition to the blue or violet rays emitted by the ordinary mixture. Other proposed mixtures are: of Mg powder + silica + boric acid (German Patent, 101,528); Al powder +  $\text{KClO}_3$  (German Patent, 101,735); Mg powder + red phosphorus + peroxides. Very powerful photo effects are obtained by adding cadmium nitrate in quantity equal to magnesium powder. Zinc nitrate also is used.

**Time Lights** do not flash, but burn slowly, an effect attained by adding to magnesium (sometimes mixed with aluminium) powder bodies such as carbonates, silicates, or oxides of the alkaline earths—*e.g.*,  $\text{SrCO}_3$ . Bayer (German Patent, 165,259) proposes Mg or Al powder +  $\text{Na}_2\text{WO}_4$ , or  $\text{WO}_3$ , as a smokeless time light. Novak proposes Mg powder + cerium nitrate +  $\text{SrCO}_3$  as a smokeless time light.

Kreb's panchromatic time lights give out coloured rays, thus enabling the taking of photographs of objects by colour sensitive plates without the use of a yellow light filter. Electric metallic filament lamps are also used now.

Although the above types of flashlights are still in use, the modern photographer has been helped considerably by several electrical devices.

The smoke produced by a flash powder is unpleasant and sparks given off are dangerous. Electrically-operated flashbulbs, containing aluminium foil or wire in an atmosphere of oxygen at low pressure, have largely displaced powders for this purpose and, owing to their glass shield, these are perfectly clean and safe. They can be obtained to operate from either mains or from batteries. The temperature of the flash is in the region of  $3,500^\circ \text{K}$ . and its duration is from  $\frac{1}{20}$  to  $\frac{1}{75}$  sec.

## DEVELOPERS

We can give here only a brief mention of some of the more important reducing substances used in the manufacture of developers.

**Iron Oxalate** is one of the oldest developers, and is still used to some extent—usually in the form of two solutions, I. and II.; I. consisting of 300 g. neutralised potassium oxalate in 1,000 c.c. of water, and II. of ferrous sulphate solution (100 g.  $\text{FeSO}_4$  + 300 c.c. water + 5 drops concentrated  $\text{H}_2\text{SO}_4$ ). For use, 3–4 parts of I. are used with 1 of II.

### Developers derived from Monohydric Phenols

**Paraminophenol**,  $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{OH} \\ \text{NH}_2 \end{smallmatrix}$  (1 : 4), produced by reducing *p*-nitrophenol with tin + HCl. Colourless crystals, M.P.  $184^\circ$ ; forms a crystalline hydrochloride,  $\text{OH.C}_6\text{H}_4.\text{NH}_2.\text{HCl}$ .

"Rodinal" contains *p*-amidophenolhydrochloride. "Unal" is rodinal in a solid form.

**Monomethylparaminophenol**,  $\text{C}_6\text{H}_4(\text{OH})(\text{NHCH}_3)$ , 1 : 4, is prepared by methylating *p*-aminophenol.

It is an excellent developer, giving results free from stain. It is known as "Scalol." Two solutions are used: (A) "Scalol," 1.5 g. + hydroquinone, 3 g. + sod. sulphite (crystals), 28 g. + KBr, 0.25 g. +  $\text{H}_2\text{O}$ , 284 c.c.; (B)  $\text{Na}_2\text{CO}_3$  (crystals), 30 g. +  $\text{H}_2\text{O}$ , 300 c.c. Use equal parts of A and B.

"Metol" is the sulphate of this body. The developer "Satrapol" also contains it. Metol works exceedingly rapidly. Stock solution: 15 g. metol + 150 g. cryst. sod. sulphite + 75 g.  $\text{K}_2\text{CO}_3$  + 2 g. KBr + 1,000 c.c.  $\text{H}_2\text{O}$ .



"Metolhydroquinone" developer, now widely used, consists of the two solutions: (A) 2 g. metol + 3.5 g. hydroquinone + 4 g.  $\text{Na}_2\text{HPO}_4$  + 400 c.c.  $\text{H}_2\text{O}$  + 2 c.c. sodium sulphite solution (1 : 100). (B) 40 g.  $\text{K}_2\text{CO}_3$  + 400 c.c.  $\text{H}_2\text{O}$ . For use, mix equal parts of A and B.

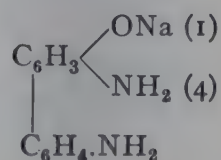
**Diaminophenol**,  $\text{C}_6\text{H}_3(\text{OH})(\text{NH}_2)(\text{NH}_2)$ , 1 : 2 : 4, is prepared by reducing with  $\text{Sn} + \text{HCl}$  1 : 2 : 4-dinitrophenol; forms salts with  $\text{HCl}$  and  $\text{H}_2\text{SO}_4$ .

"Amidol" consists of 20 g. diaminophenol sulphate or chloride + 200 g. cryst. sod. sulphite + 1,000 c.c.  $\text{H}_2\text{O}$ . Solution will not keep. Best developer for bromides and gaslight papers. Valenta proposes acetonesulphite + diaminophenol hydrochloride as a powerful developer.

**p-Amino-saligenin**,  $\text{C}_6\text{H}_3(\text{CH}_2\text{OH})(\text{OH})(\text{NH}_2)$ , 1 : 2 : 3, in the form of its hydrochloride, occurs as an easily soluble white powder, similar in properties to amidol, but having the advantage of allowing very concentrated solutions being formed.

"Edinol" (made by Fr. Bayer, Elberfeld) consists of 5 g. p-amino-saligenin + 7.5 g. acetone sulphite + 30 g.  $\text{KOH}$  + 0.5 g.  $\text{KBr}$  + 100 c.c.  $\text{H}_2\text{O}$ . Edinol-hydroquinone developer consists of 2 g. p-amino-saligenin + 1 g. hydroquinone + 5 g. acetone sulphite + 30 g. cryst. sod. sulphite + 30 g.  $\text{K}_2\text{CO}_3$  + 150 c.c.  $\text{H}_2\text{O}$ .

**Diamino-hydroxydiphenyl**, in the form of its sodium salt, is used in a manner similar to "Rodinal." Placed on the market under the name "Diphenal" by Cassella & Co.



**p-Hydroxyphenylglycocoll**,  $\text{C}_6\text{H}_4(\text{OH})(\text{NH}.\text{CH}_2.\text{CO}_2\text{H})$ , 1 : 4, is manufactured by heating p-aminophenol,  $\text{C}_6\text{H}_4(\text{OH})(\text{NH}_2)$ , with monochloroacetic acid,  $\text{CH}_2\text{Cl}.\text{COOH}$ , in aqueous solution.

Used as a developer, it gives pure black tones and keeps well. It is placed on the market as "Glycin." Stock solutions are: 5 g. glycin + 25 g. cryst. sod. sulphite + 100 c.c.  $\text{H}_2\text{O}$  + 25 g.  $\text{K}_2\text{CO}_3$ . Another good keeping solution is 2 g. glycine + 800 c.c.  $\text{H}_2\text{O}$  (recently boiled) + 2 g. cryst. sod. sulphite + 15 g.  $\text{K}_2\text{CO}_3$ . It is used chiefly for stand development because it does not produce chemical fog by long action.

**Methylorthoaminophenol**,  $\text{C}_6\text{H}_4(\text{OH})(\text{NHCH}_3)$ , 1 : 2, 2 molecules of which, combined with 1 molecule of hydroquinone, forms the basis of the excellent developer "Ortol."

Two naphthalene compounds are used as developers:—

**Sodium  $\alpha_1$ -amino- $\beta_1$ -naphthol- $\beta_3$ -sulphonate**,  $\text{C}_{10}\text{H}_5(\text{OH})(\text{NH}_2)(\text{SO}_3\text{Na})$ , a good developer if used at 20° C. or a little below. It forms the basis of Eikonogen, one of the best developers for plates which have received very short exposure.

Hydroquinone-eikonogen developer consists of two solutions, A and B: (A) 100 g. cryst. sod. sulphite + 16 g. eikonogen + 4 g. hydroquinone + 900 c.c. boiling water; (B) 40 g.  $\text{K}_2\text{CO}_3$  + 200 c.c.  $\text{H}_2\text{O}$ . For use, 40 c.c. of A are added to 180 c.c. B, together with 3 drops 10 per cent.  $\text{KBr}$  solution.

**Sodium aminonaphtholdisulphonate**,  $\text{C}_{10}\text{H}_4(\text{NH}_2)(\text{OH})(\text{SO}_3\text{Na})_2$ , which forms the basis of the developer "Diogen."

**Glycin** (p-hydroxyphenylaminoacetic acid),  $\text{C}_6\text{H}_4\text{OH}.\text{CH} : \begin{cases} \text{NH}_2 \\ \text{COOH} \end{cases}$ , is a white crystalline powder, very slightly soluble in water but freely soluble in alkaline

solutions. A glycin developer keeps better than any other but is usually considered too slow in action for general use. It is used in some fine-grain developers.

***p*-Phenylenediamine** (diaminobenzene). Many popular fine-grain developers consist of *p*-phenylenediamine and sodium sulphite with varying concentrations of glycin. One such compound is "Meritol."

### Developers derived from Dihydric Phenols

**Hydroquinone**,  $C_6H_4(OH)_2$ , 1 : 4, is a developer much used by amateurs, giving strong hard negatives of a bluish black tone.

The best preparation occurs as yellowish crystals, and is obtained by recrystallising the commercial product in the presence of  $SO_2$ . The stock solution consists of 5 g. hydroquinone + 40 g. cryst. sod. sulphite + 6.5 g. KOH + 150 c.c.  $H_2O$ . It is frequently combined with other developers. See **Edinol**, **Eikonogen**, **Metol**.

**Monochlor- and Monobromhydroquinones**,  $C_6H_3Cl(OH)_2$  and  $C_6H_3Br(OH)_2$ , are now used as developers under the name "**Adurol**" (see German Patent, 111,798).

Monochlorhydroquinone is obtained by leading Cl gas through hydroquinone dissolved in benzol, while the bromo derivative is obtained by adding a solution of Br in benzol to a hydroquinone benzol solution, evaporating the benzol and crystallising from ligroin.

"Adurol" developer consists of the stock solutions: (A) 10 g. adurol + 80 g. cryst. sod. sulphite + 500 c.c.  $H_2O$ ; (B) 60 g.  $K_2CO_3$  + 500 c.c.  $H_2O$ . One part A, one part B, and one part  $H_2O$  are taken to develop. Adurol comes between hydroquinone and the "rapid developers" (metol, rodinal, etc.) in properties. It does not turn brown by oxidisation in air, and so may be repeatedly used.

**Pyrocatechol**,  $C_6H_4(OH)_2$ , 1 : 2, has been proposed as a developer, and under the name "Kachin" has been placed on the market.

**Resorcin**,  $C_6H_4(OH)_2$ , 1 : 3, is of no use as a developer. Two amino derivatives of it, however, are used for this purpose, namely, **Diaminoresorcin**,  $C_6H_2(NH_2)_2(OH)_2$  (4 : 6) (1 : 3), and **Triaminoresorcin**,  $C_6H(NH_2)_3(OH)_2$  ("Reducin").

### Developers derived from Trihydric Phenols

**Pyrogallol**,  $C_6H_3(OH)_3$  (1 : 2 : 3), is the basis of most of these. Pyrogallol developers work rapidly, but have the drawback that they stain the fingers, are poisonous, and do not keep well.

**Pyrosoda Developer**.—Stock solutions: (A) 10 g. pot. metabisulphite + 83 g. pyrogallol + 13 g. KBr + water up to 1,000 c.c.; (B) 100 g.  $Na_2SO_3$  + 100 g.  $Na_2CO_3$  +  $H_2O$  up to 1,000 c.c. For use, mix 1 part A with 1 part B and 1 part  $H_2O$ .



**Pyropotash Developer.**—Stock solutions: (A) 25 g. cryst.  $\text{Na}_2\text{SO}_3$  + 100 c.c.  $\text{H}_2\text{O}$  + 10 g. pyrogallol + 3-4 drops  $\text{H}_2\text{SO}_4$ ; (B) 45 g.  $\text{K}_2\text{CO}_3$  + 12.5 g.  $\text{Na}_2\text{SO}_3$  in 100  $\text{H}_2\text{O}$ . Use 3 c.c. A and 3 c.c. B with 100 c.c.  $\text{H}_2\text{O}$ .

**Pyrometol.**—Stock solutions: (A) 5 g. metol + 14 g. pot. metabisulphite + 6 g. pyrogallol + 2 g.  $\text{KBr}$  +  $\text{H}_2\text{O}$  up to 1,000 c.c.; (B) 200 g.  $\text{Na}_2\text{CO}_3$  + 1,000 c.c.  $\text{H}_2\text{O}$ . Use equal quantities of A and B. Gives a good printing yellow negative.

“**Pinakol P**” is an excellent developer made by replacing in the pyropotash developer the alkali by half the equivalent amount of **sodium aminoacetate**,  $\text{CH}_2\text{NH}_2\text{COONa}$ . Developing with “Pinakol P” gives stronger, clearer, and more rapid results than the old pyro developers; moreover, it does not stain the fingers.

**Pinakol Salt N** is a 20 per cent. solution sodium aminoacetate,  $\text{CH}_2\text{NH}_2\text{COONa}$ . It is used for replacing alkali in organic developers since it does not affect the skin of the operator and the gelatine film in the unpleasant way that alkali does; moreover the results attained are superior to those of soda and potash.

**Acetone bisulphite, acetone-sulphite “Bayer,”** is now largely used as a substitute for sodium or potassium bisulphite in developers. It is antiseptic, a restrainer for rapid developers, a clearing agent for fixing baths and developing papers, and is used also for darkening the negative after the use of mercury intensifiers.

## FIXING, TONING, AND COMBINED BATHS

**Sodium Thiosulphate**,  $\text{Na}_2\text{S}_2\text{O}_3 + 5\text{H}_2\text{O}$ , is now practically the only fixing salt used. The fixing occurs according to the equation:—



the  $\text{Ag}_2\text{S}_2\text{O}_3$  then combines with the excess of  $\text{Na}_2\text{S}_2\text{O}_3$  to form the soluble double salt  $\text{Ag}_2\text{S}_2\text{O}_3 \cdot 2\text{Na}_2\text{S}_2\text{O}_3$ .

The thiosulphate may be used in neutral solution (1 : 4  $\text{H}_2\text{O}$ ) but is best used in acid bisulphite fixing solution, and sometimes alum is added (to harden the gelatine).

The following are well-known gold **toning** baths:—

**Ordinary Toning Bath.**—(A) 4 g. borax in 1,000 c.c.  $\text{H}_2\text{O}$ ; (B) 4.5 g. anhydrous sodium acetate in 1,000 c.c.  $\text{H}_2\text{O}$ ; (C) 1 g. gold chloride in 50 c.c.  $\text{H}_2\text{O}$ . Use 8-10 c.c. of C + 100 c.c. A + 100 c.c. B.

**Neutral Toning and Fixing Bath.**—250 g. sodium thiosulphate + 20 g. lead acetate + 10 g. calcium chloride + 0.4 g. gold chloride + 1,000 c.c.  $\text{H}_2\text{O}$ .

**Acid Toning and Fixing Bath.**—250 g. sodium thiosulphate + 25 g. ammonium sulphocyanide + 10 g. lead acetate + 5 g. citric acid + 0.4 g. gold chloride + 1,000 c.c.  $\text{H}_2\text{O}$ .

Platinum toning baths are also used, the basis being  $\text{PtCl}_4$  or  $\text{PtCl}_2$ , which reacts with Ag salts thus:  $4\text{Ag} + \text{PtCl}_4 = 4\text{AgCl} + \text{Pt}$ .

**Palladium Chloride**, used as a toning bath for silver pictures, gives beautiful brown tones.

**Sodium Thiosulphate Destroyers.**—A lengthy washing is required to remove the last traces of sodium thiosulphate, and the durability of the print largely depends on its complete removal. Consequently attempts have been made to find substances which rapidly destroy the last traces of thiosulphate. The best known substances are **Anthion** = potassium persulphate, **Thioxydant Lumière** = ammonium persulphate. More recently **percarbonates**, **perborates**, and **permanganates** have been suggested.

Bayer’s “Hypo-destroyer” = persulphate + percarbonate. “Antihypo” is potassium percarbonate. 10 g. are dissolved in 1,000 c.c.  $\text{H}_2\text{O}$  and the plates and paper, after rinsing, are immersed for a few minutes after which only a short rinsing is necessary. A great time-saving is thus effected.

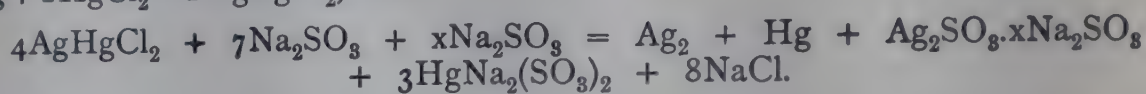


## REDUCERS AND INTENSIFIERS

**Reducers** are chemicals which act by dissolving the fine silver particles. A large number of such substances are known, being oxygen-rich substances such as chromic acid, mercuric nitrate, ferric-, manganic-, ceric-, and titanous-salts, persulphates, etc.

*Farmer's* reducer = 100 c.c. sodium thiosulphate solution 1:4 + 8 c.c. of a 10 per cent. potassium ferricyanide solution. This destroys the fine middle tones, and so increases the contrasts. **Ammonium persulphate reducers** diminish the contrasts by acting on the darker parts of the plate. **Cerium sulphate** makes a very uniform reducer.

**Intensifiers** are used to increase the density of thin negatives, and bring out the contrasts better. The **mercury intensifying process** consists in treating the negative with a solution containing 2 per cent. mercuric chloride + 2 per cent. KBr. When the negative is grey it is removed, rinsed, and immersed in a 12 per cent. solution of sodium sulphite, when the negative becomes black again:  $2\text{Ag} + 2\text{HgCl}_2 = 2\text{HgAgCl}_2$ , then



The **uranium** intensifying process requires two solutions: (A) 1 g. uranium nitrate + 100 c.c.  $\text{H}_2\text{O}$ ; (B) 1 g. potassium ferricyanide + 100 c.c.  $\text{H}_2\text{O}$ . For use, 50 c.c. A + 11 c.c. acetic acid + 50 c.c. of B are mixed. Other intensifying solutions used are:  $\text{CuSO}_4$  + pot. ferricyanide + pot. citrate, and  $\text{HgI}_2 + \text{Na}_2\text{SO}_3$ . Intensifiers containing **bichromate** are also used.

## PHOTOGRAPHIC PAPERS

An enormous number of these exist: we may class them into—

**1. Printing-out Papers.**—The p.o.p. papers are still made (although developing papers have largely supplanted them) and usually employ silver chloride as the sensitive substance. Four well-defined groups of papers are manufactured: (a) **Albumen papers**, in which the ground is albumen and the sensitive substance silver chloride. (b) **Silver chloride gelatine paper**; here the ground is gelatine and the sensitive substance silver chloride. (c) **Silver chloride collodion papers**. (d) **Silver chloride casein papers** give good results and resist high temperatures. Direct printing platinum papers are also on the market.

On exposure to light the chloride is converted to a "photo-chloride,"  $\text{Ag}_2\text{Cl}$ , of a purple or reddish colour, and stated to be an adsorption compound of silver chloride and silver, of variable composition. After the paper has been printed the colour of the deposit is modified by immersion in a bath containing a gold or platinum salt, associated with a weak reducer, so that metallic gold or platinum is precipitated ("Toning"). The unused silver chloride,  $\text{AgCl}$ , is then dissolved out by thiosulphate ("Fixing"), which only slightly attacks the photo-chloride.

**2. Developing Papers.**—These may also be grouped into five classes, namely: (a) **Silver bromide papers** consisting of an emulsion of silver bromide + gelatine; used for printing and enlargements; very sensitive and must be worked in a dark room. (b) **Silver chlorobromide papers** can be used for printing in ordinary shaded daylight or by gaslight. (c) **Silver phosphate papers** may be printed in weak daylight or by gaslight. When developed they give p.o.p. effects. (d) **Platinum** developing papers give excellent results. (e) **Pigment papers** are covered with chromogelatin, which under the influence of light becomes insoluble in hot water. As any pigment can be mixed with the gelatine very beautiful



coloured results are obtainable. In the bromoil process the bleached bromide print is worked up with special inks.

The chief difference between emulsions for development papers and those for plates is that paper emulsions are of a much lower sensitiveness (finer grain), and contain a larger proportion of silver to gelatine, the coating being thin so as to keep the image on the surface of the paper. The colour of the image obtained depends upon the size of the grain, and developers can be used by which the silver is deposited in a very finely divided state, almost approaching to colloidal solution. By the admixture of such fine grain silver with larger grains, various tones can be obtained upon development. The papers, which are sometimes faced with  $\text{BaSO}_4$ , are manufactured by passing through a trough containing the emulsion. The paper is not actually dipped under the surface of the emulsion in the coating trough, but the paper is carried around a roll under tension, and the emulsion is beaded on to the paper. In other words, the paper lightly touches the surface of the emulsion in the trough, the beading being a capillary action; then over a cold roller to set the gelatine, then hung up in loops in a long drying chamber, through which it slowly travels, emerging dry after about two and a half hours. It is then rolled direct and cut. Surface-coated papers without gelatine, such as platinum papers, are dried almost instantly on a short machine by hot air, and do not require the elaborate hanging and slow drying arrangements used for gelatine-coated papers.





SECTION XXIV

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The Tobacco Industry





# THE TOBACCO INDUSTRY

BY S. E. HODGKINSON,

Tobacco Work's Chemist, author of article "Tobacco," in  
Atack's "Chemist's Year Book."

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ALLEN'S "Commercial Organic Analysis."

## Historical Survey

THE smoking of the leaves of the tobacco plant may be definitely stated to be of American origin, and it is thought that at first it probably was a religious rite. Many attempts have been made to prove that the custom was practised by the ancient Egyptians, the Greeks, and Romans, and in the East generally, prior to the discovery of America, but it has been conclusively shown that the herb smoked was not tobacco, but generally coltsfoot. During the seventeenth century, when the use of tobacco was spreading over Europe, smoking was prohibited in India, Turkey, and Persia, under penalty of death, and from this process of elimination we return to the known fact that smoking was everywhere practised by the natives when America was first discovered to Europeans. Fairholt, in his work on the "History of Tobacco," states that it was in the first week of November 1492 that Europeans first noted this Indian custom on the island of Cuba. The first clear account of the practice is given by Oviedo in his "Historia General de las Indias," published in 1526. In the West Indian islands the natives smoked rolls of leaves, something like our modern cheroots, but on the mainland a hollow Y-shaped nose pipe, called a "Tobago," was used. The herb itself was named "Appowac."

Though well known to Columbus and all the Europeans subsequently visiting America, the herb was only introduced into Europe about 1560 by Hernandez de Toledo, a physician sent by Philip II. of Spain to investigate the products of Mexico. About the same time Jean Nicot introduced it into France, and about 1586 Ralph Lane, one of Sir Walter Raleigh's lieutenants, first brought it to England. So rapidly did the practice spread, that early in the seventeenth century it was fiercely assailed, James I. raising the duty on tobacco from 2d. to 6s. 10d. per pound. This advance of 4,000 per cent., however, only applied to colonial-grown tobacco, Spanish and Portuguese tobacco being imported for many years at the 2d. duty, also the leaf began to be cultivated in England to evade the tax; but in 1621 James passed a measure prohibiting its cultivation, as to do so would "misuse and misemploy the soyle of this fruitfull kingdom." The smoking of tobacco was never directly prohibited in England, as in many countries.

**Statistics.**—In 1913 the total imports of tobacco and cigars into the United Kingdom amounted to 165,365,925 pounds, 3½ million pounds of which was manufactured. Of the 162 million pounds of leaf imported, 142 million pounds came from the United States.

For modern statistics see Appendix III.

## Growth and Curing

The smoking tobacco of commerce is the dried and prepared leaves of some three species of the genus *Nicotiana*, natural order *Solanaceæ* (Deadly Nightshade family).

A very large number of species are known to botanists, but only three are of commercial importance—*Nicotiana tabacum*, *N. rustica*, and *N. persica*.



The first of these, the original American plant, is by far the most important. The familiar tobacco plant of English gardens, *N. affinis*, is not cultivated for smoking purposes. Over seventy varieties of *N. tabacum* are mentioned by Killibrew and Myrick as being cultivated in the United States. It is now grown in many parts of the world, and provides about seven-eighths of all the tobacco consumed. *N. rustica* is cultivated in Europe, Asia, and Africa, and grows wild (as a perennial) in certain parts of Mexico. It is a hardier plant than *N. tabacum*, with small oval leaves, attached to the parent stem by means of a stalk. Turkish, Syrian, Hungarian, and Latakia varieties are from this species. *N. persica* is usually found in Persia. It gives rise to an exceedingly mild variety of tobacco known as *Shiraz*.

Although a perennial, tobacco is raised from seed annually.

The plant (*N. tabacum*) grows from two to nine feet high, according to variety, with wide spreading leaves, ovate or lanceolate in form. The leaves, which at their base enwrap the parent stem, forming the familiar "spur" at the butt-end of the dried leaf (distinction from *N. rustica*), are alternately attached to the stalk spirally, so that the ninth leaf overhangs the first. The flowers are in large clusters, usually of a pinkish colour. The leaves and stalks are covered with soft, downy hair.

Tobacco flourishes in a temperate climate, the best soil being alluvial or light loam, with plenty of potash.

From experiments conducted by the United States Department of Agriculture (Dr W. W. Garner and others) it is shown that *fertilisers* have a very marked influence on the plant, especially on the composition of the ash, and consequently upon the combustibility, which depends largely upon the nature and state of combination of the inorganic constituents. Potash, and magnesia in small quantity, improve the "burn"; lime, also in moderate quantity, is beneficial, and tends to whiten the ash. Chlorine and sulphates inhibit the burn, and for these reasons potassium sulphate and stable manure are not very satisfactory manuring agents, the latter imparting too much chlorine to the tobacco. The bad effect of chlorine would seem to be neutralised by an excess of potash. It is usual to burn brushwood on a field to be used for tobacco growing, afterwards digging in the ash. (See Killibrew and Myrick, "Tobacco Leaf"; W. W. Garner, "The Relation of the Composition of the Leaf to the Burning Qualities of Tobacco," Dept. of Agric., Washington, 1907; Henry and Auld, *Bull. Imp. Inst.*, 1910, 8, 142.)

Heavy manuring of tobacco lands with suitable fertilisers is essential to the growing of good crops, otherwise the ground becomes exhausted, and as the main period of growth lasts only for ten or twelve weeks in the summer, the plant food must be in a more available form than would be necessary with crops of a more extended period of growth. Consequently heavier and more careful manuring is required in northern districts than in those where the summer lasts longer, in order that the plant may reach maturity.

Very few plants are as susceptible to culture and climatic conditions as tobacco. It has been stated that leaf grown from seed of the fine textured Cuban cigar tobacco, planted in the more northern parts of the United States, in a very few generations becomes changed to a thick-textured tobacco totally different from the Cuban leaf, even when every care is taken to prevent cross-fertilisation, to which the different varieties of *N. tabacum* are particularly prone. So prone, indeed, is the plant to cross-fertilisation, that in order to keep a desirable variety from deterioration it is essential that no two varieties be grown on the same farm.

By the operation of these three variants—soil, climate, and cross-fertilisation—hundreds of modifications have been secured. Cross-fertilisation between totally different varieties is often resorted to in order to improve the stock. Some of Darwin's classical experiments were done on tobacco.

With the above reservations, the actual growing of tobacco is an ordinary agricultural operation.

Only from eight to ten leaves are allowed to mature on the plant, and generally it is "topped," i.e., the flowering stem is removed before the flower appears. Suckers must also be removed as they appear.

The curing and fermentation or sweating of tobacco are processes requiring much knowledge and experience, and great technical ability. The methods employed vary in different states and with different varieties. In brief outline the general process is as follows:—



When the crop is ripe the plant is cut down, carefully laid on the ground, and exposed to the heat of the sun until it becomes wilted and flaccid. In some districts the leaves are harvested separately as they ripen, and some varieties of leaf require to be taken to the curing barns with the least possible delay. Too long exposure to the sun after being cut injures the crop, so a hot cloudy day is generally chosen for the harvesting. Whichever method of harvesting is adopted, the crop is ultimately placed in specially constructed drying sheds, where it is either air-dried ("sun-cured") or dried by heat equally distributed through the shed by means of flues. Some varieties of tobacco are dried by means of open fires of sassafras and hickory wood, the smoke being allowed to pass among the hanging leaves, imparting to the tobacco an odour somewhat resembling creosote. During this process there is a decrease in the dry matter of the leaf, as well as in the moisture. The starch is turned to glucose (which latter is finally dissipated as carbon dioxide, water, etc., in the later process of sweating or fermentation). At this stage there is no loss of nitrogen, though the albuminoids are split up into asparagine and other amides. These changes are sometimes stated to be merely due to drying and oxidation, but Frear ("Tobacco Leaf") has shown that, although not due to micro-organisms, they are the result of life action, as the changes only occur while the protoplasm of the leaf cells retains life. If the leaf be frozen or chloroformed the protoplasm is killed, and no normal curing can then be effected. The control of temperature during curing is very important.

The following methods, employed by Mr R. L. Ragland, of Virginia, is given as an example:—

1. The "sapping" process. As soon as cut the tobacco is put under a temperature of 90° F. for three hours, then the temperature is advanced rapidly to 125° F., or as high as the tobacco will stand without scalding. After a few minutes the temperature is allowed to fall to 90° again. This opens the cells and allows the water to come to the surface.
2. The yellowing process, requiring 90° for from four to eight hours.
3. Fixing the colour, requiring from sixteen to twenty hours at a temperature ranging from 100° F. at the beginning to 120° F. at the close.
4. The curing process, requiring a temperature of 120°-125° F. for forty-eight hours.
5. The curing of the stalk and stem, requiring from nine to ten hours, with a heat of 125°-175° F., increased at the rate of 5° an hour.

On the first ensuing damp day after the leaves have become dry and brittle, air is freely admitted to the shed, when the tobacco absorbs sufficient moisture to become pliable. It is taken down from the tiers of poles upon which it has been hanging, stripped from the parent stem, if this operation has not already been performed, and graded. The slightly moist tobacco is heaped together in piles on the floor of the barn, the temperature rises, and the tobacco is said to "sweat" or "ferment." When the temperature reaches 130° F. the pile is reformed, with the leaves in the centre which were formerly on the outside.

By cooling the vapours given off during the fermentation, M. Betting (*J.S.C.I.*, 1910, 520) obtained a strongly alkaline liquid of sp. gr. 0.0998 at 27.5° C., in which the presence of ammonia, nicotine, ethyl alcohol, and acetone were detected.

The precise nature of the fermentative process has been much discussed.

Following Nessler ("Der Tabac," 1867), it is generally stated to be due to bacteria. Behrens ("Centralblatt. für Bakteriologie und Parasitenkunde," 11, 1894, p. 335 *seq.*) endeavoured to ascertain the changes which occur during sweating. He found the loss of dry matter to be from 2.5-5.6 per cent., chiefly of soluble carbohydrates, and some organic acids. Although there was no diminution of total nitrogen (but see Garner, quoted below), one-third of the nicotine disappears, and there is a loss of nitrate nitrogen. He believed these changes to be due chiefly to the action of anaerobic ferments. Jensen (*J.S.C.I.*, 1908, 1181), and Boekhout and de Vries (*J.S.C.I.*, 1909, 1277), deny that this view is correct, and state that the process is of a purely chemical character.

During the processes of curing and sweating, the tobacco attains the familiar rich brown colour. The objectionable albuminoids are broken down, about one-fourth of the nitrogenous constituents disappearing, ammonia being liberated in appreciable amounts, and excess of free or loosely combined nicotine eliminated. (W. W. Garner, "The Relation of Nicotine to the Quality of Tobacco," Washington, 1909; Bernardini, *J.S.C.I.*, 1915, 300.)

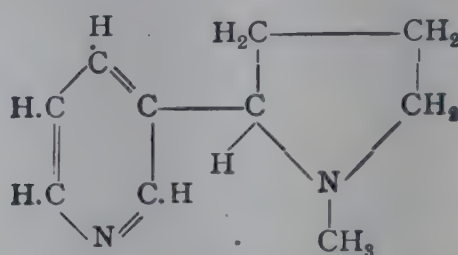


## Constituents of Tobacco Leaf

When first cut down the tobacco plant contains 85-95 per cent. of water, and even as imported the so-called dry leaf contains from 13-20 per cent. of moisture, normally about 14 per cent.

Nicotine ( $C_{10}H_{14}N_2$ ) is the active principle peculiar to tobacco. It occurs combined with malic, citric, and other organic acids, and also in unfermented or insufficiently fermented tobacco, in the free and loosely combined state (W. W. Garner). It was discovered by Passelt and Reiman in 1828, its constitution first determined by Pinner, and it was prepared synthetically by Pictet, who confirmed its constitutional formula in 1904.

Pure nicotine is a colourless oily liquid, with a sharp burning taste, and a faint ethereal odour. On exposure to air it becomes brown, and acquires the strong pungent odour of tobacco. It is freely soluble in water, alcohol, and the usual organic solvents. It boils at  $247^\circ\text{C}$ . (with decomposition), but may be distilled in a stream of hydrogen or in a current of steam, or under reduced pressure. Its specific gravity at  $15^\circ\text{C}$ . is 1.011, and it is optically active, the naturally occurring alkaloid being lævorotatory,  $[\alpha]_{\text{D}}^{20} = -161.55^\circ$ . A method of estimation based on this fact has been devised by Degrazia (*J.S.C.I.*, 1911, 506). Chemically, it is  $\beta$ -pyridyl-N-methylpyrrolidine:—



It is a strong base, forming salts with both organic and inorganic acids. It is an excessively poisonous substance, six milligrammes having been suggested as probably the fatal dose for an adult (*A. Wynter Blyth*).

It affects the nervous system, increases the activity of the secreting glands, and causes constriction of the blood vessels. It first raises the blood pressure, then diminishes it, and contracts the walls of the stomach, causing nausea and vomiting. Convulsions usually occur, death resulting finally from paralysis of the central nervous and respiratory systems.

In cases of poisoning by nicotine the stomach is evacuated and tannic acid given, which, being an astringent, inhibits absorption, and in addition forms an insoluble compound. Stimulants such as caffeine and strychnine then follow.

It has been used medicinally on rare occasions as an antidote to strychnine poisoning, and in tetanus.

Nicotine salicylate is said to be sold under the trade name of "*Eudermole*" as a parasiticide, chiefly used as an ointment.

The salts which nicotine forms with non-volatile acids (malic, succinic, citric, oxalic, sulphuric) are themselves more or less non-volatile and insoluble in petroleum ether, whilst the salts formed with volatile acids (acetic, hydrochloric) are volatile and soluble in petroleum ether. Nicotine is readily removed from petroleum ether extract by agitating with aqueous sulphuric acid, the nicotine sulphates formed being soluble in water, but insoluble in petroleum ether.

**Uses.**—The chief use of nicotine and its preparations is as an insecticide in horticulture, a solution in water of 0.075 per cent. strength being a most efficient spray for the destruction of certain insect pests infecting plants, while it has no equal as regards its power of destroying the sheep scab mite and certain other animal parasites (*Edwards-Ker*, "The Growing of Tobacco for Nicotine Extraction," S.E. Agric. Coll., Wye, Kent). For this purpose it is prepared by allowing water to percolate through hoppers filled with waste tobacco, the extract made alkaline, and distilled in a current of steam. Sulphuric acid is added to the distillate, and after evaporation the nicotine sulphate is decomposed by caustic soda and the nicotine distilled off.

The use of nicotine in the plant economy appears to be doubtful, but it is regarded as being derived from the protein matter. Its percentage varies in different parts of the plant and at different stages of its growth, but in all parts except the seed, and at all stages, some nicotine is present. *Pannain* (*J.S.C.I.*, 1915, 246) has shown that if the ripe leaves are picked as they mature, the third and fourth pickings contain only half as much of the alkaloid as the first and second. The amount of ash also decreases from the first to the fourth picking. The leaf blades are richer than the midribs in every constituent except organic acids, and this holds good for the whole leaf in comparison with the stem and roots. Although the percentage of nicotine varies with the variety (from less than 1 per cent. in Syrian to 7 per cent. in Kentucky), the nature of the soil, climatic conditions, and the character of the manure used exert a very considerable influence on its production in the plant. The conditions which tend to produce a coarse, rank growth tend



also to produce a high nicotine content. Acting upon this knowledge tobacco has been grown in England solely for the purpose of extracting the alkaloid (*Garrod and Edwards-Ker*, "The Growing of Tobacco for Nicotine Extraction"). Such tobacco pays no excise duty, but it must be suitably denatured before passing out of excise control.

A high nicotine content in smoking tobacco is undesirable, and it is generally considered that the aroma and flavour are dependent upon a volatile substance called nicotianin, or tobacco camphor, which exists in the leaf in inverse ratio to the nicotine content. The amount of this substance present is very small, being about 0.2 per cent. of the dry weight.

Its constitution has been the subject of some discussion. *Gerhardt*, working upon the percentage composition found by *Barral*, ascribed to it the formula  $C_{23}H_{32}N_2O_2$  (*J.S.C.I.*, 1902, 797), but *Gawalowski* (*J.S.C.I.*, 1902, 1348) states that the so-called tobacco camphor is a mixture of the nicotine salts of valeric, camphoric, oxycamphoric, and pyridyl-carboxylic acids, nicotine pyridyl-carbonate being the chief toxic principle, whilst the aroma is due to the other three salts mentioned. Small traces of other alkaloids have been detected in tobacco, namely, nicotine, isonicotine, nicotelline, nicotone ( $C_8H_{11}N$ ), pyrrolidine, and methyl-pyrrolidine (*Redgrove* (*Knowledge*, 1914, 46); *Pictet and Rotschy* (*J.S.C.I.*, 1901, 501); *E. Noga* (*J.S.C.I.*, 1915, 979)). *Thorpe and Holmes* (*Chem. Soc. Trans.*, 1901, 79, 982) isolated two hydrocarbons, hentriacontane,  $C_{31}H_{64}$ , M.P.  $67.8^\circ-68.5^\circ$  C., and heptacosane,  $C_{27}H_{56}$ , M.P.  $59.3^\circ-59.8^\circ$  C., and recently *Halle and Pribram* (*J.S.C.I.*, 1914, 612), an essential oil has been isolated in 0.047 per cent. yield. Tobacco also contains a comparatively large amount of wax and resins. The chemistry of these latter substances has been investigated by *J. von Degrazia* (*J.S.C.I.*, 1914, 436; 1915, 978), and the following constituents isolated:  $\alpha$ -tobakenic acid,  $\beta$ -tobakenic acid, tobacco resinol, tobacco resene, and an essential oil.

*Fesca and Imai* (*J.S.C.I.*, 1888, 759), in an investigation of the modes of the existence of nitrogen in tobacco, state that nitric acid and carbohydrate should not be present in well-fermented tobacco, though amines may be harmless or even beneficial, the conversion of proteids into amines being one of the most important results of fermentation. High basicity of the ash is a good index of combustibility. Very much magnesia is prejudicial to the burn.

*Ampolo and Jovino* (*J.S.C.I.*, 1902, 997) state that the direct factors governing the combustibility of tobacco are the state of division of the metals present, especially iron, which are capable of exerting a catalytic action. A recent paper by *G. Paris* (*J.S.C.I.*, 1917, 666) critically examines the various methods proposed for the estimation of nitrogenous substances in tobacco—nicotine, ammonia, nitric acid, amines, aspartic acid, etc.

Barium, arsenic, titanium, and other rare metals have been detected in the ash of tobacco.

In common with other vegetable substances, tobacco also contains starch (usually in small quantity), sugar (only in unfermented tobacco, except for small quantities of a readily hydrolysable allatoin glucoside (*Ampolo and Scurti*, *J.C.S.*, 1909, vii., 339)), woody fibre, or cellulose, albuminoids (or amines), in addition to organic acids and mineral constituents. (See tables subjoined.)

#### PERCENTAGE COMPOSITION OF AMERICAN TOBACCO

Dried at  $100^\circ$  C. (*G. E. Moore*)

	Virginia Sun-Cured.	Virginia Flue-Cured Low Grade.	Clarksville Fire-Cured. Soil: Heavy Rich Loam.	Kentucky Air-Cured.	Perique.	Wisconsin Seed Leaf.
	1	2	3	4	5	6
Nicotine - - -	3.26	4.30	5.29	3.12	4.32	0.86
Resin and fats - - -	4.15	4.65	4.99	5.34	6.28	3.28
Starch - - -	5.89	2.75	3.54	4.45	2.45	4.15
Glucose - - -	6.89	2.75	...	...	...	...
Albuminoids (Nx 6.25) - - -	16.09	13.66	16.54	15.98	15.80	20.34
Pectic acid (anhydride) - - -	6.19	7.46	6.01	7.49	6.66	11.61
Citric " " - - -	2.12	2.84	2.99	4.05	1.18	2.99
Malic " " - - -	5.02	7.58	5.51	9.26	3.94	6.88
Oxalic " " - - -	0.84	1.03	1.30	2.18	3.49	1.07
Acetic " " - - -	0.42	0.55	0.39	0.64	1.62	0.68
Nitric " " - - -	...	...	1.55	...	...	1.22
Ammonia - - -	0.33	0.32	0.98	0.48	0.76	0.63
Crude fibre - - -	9.58	9.24	9.68	12.18	9.08	12.97
Sand - - -	0.55	2.38	2.25	0.66	4.17	1.53
Ash (exclusive of sand and $CO_2$ )	12.41	13.36	14.37	16.06	13.30	15.43
Undetermined - - -	26.26	27.13	24.61	18.11	26.95	16.36



## ASH ANALYSIS

	Virginia Sun-Cured.	Virginia Flue-Cured Low Grade.	Clarks- ville Fire-Cured. Soil: Heavy Rich Loam.	Kentucky Air-Cured.	Wisconsin Seed Leaf.
Total ash - - - - -	14.29	17.42	19.23	21.85	20.81
Ash (exclusive of sand and CO <sub>2</sub> ) - - - - -	12.41	13.36	14.37	16.06	15.43
Potash - - - - -	34.16	26.55	33.15	39.51	38.71
Soda - - - - -	0.26	0.22	0.15	0.86	1.08
Lime - - - - -	31.76	36.96	36.48	39.80	33.49
Magnesia - - - - -	7.91	11.51	11.85	5.34	12.57
Ferric oxide - - - - -	0.58	0.95	0.51	1.56	0.79
Alumina - - - - -	1.22	1.81	0.95	0.51	0.74
Manganous oxide - - - - -	...	...	0.25	0.13	trace
Phosphoric anhydride - - - - -	3.81	3.23	4.42	6.09	3.09
Sulphuric - - - - -	4.99	4.27	6.16	4.52	3.89
Silicic - - - - -	1.39	3.29	3.42	1.20	4.65
Chlorine - - - - -	13.92	11.21	2.66	0.48	0.99

The constitution of tobacco smoke has been the subject of considerable investigation, particularly by *Töth* (*J.S.C.I.*, 1910, 458), *Thoms* (*J.S.C.I.*, 1901, 626), *Trillat* (*J.S.C.I.*, 1904, 1164), and *Garner* ("Relation of Nicotine to the Quality of Tobacco"). It has been found to contain, in addition to unchanged oxygen and nitrogen from the air, carbon dioxide, carbon monoxide, formaldehyde, ammonia, hydrogen sulphide, hydrogen cyanide, butyric acid, pyridine, collidine, and nicotine; also two volatile oils in minute proportions (75 parts in 20,000), one of which is extremely toxic. According to *Garner*, 25-35 per cent., and according to *Thoms* about 75 per cent. of the nicotine present in the tobacco passes into the smoke. That is to say, taking the lower figure of *Garner*, in smoking an average cigar weighing 5 gm. made from tobacco containing 2 per cent. of nicotine, 25 mg.—four times the minimum fatal internal dose—of this alkaloid are drawn into the mouth. It would be of interest to ascertain whether the hydrogen cyanide takes any part in the physiological effect produced by tobacco smoking.

An interesting paper on the relative toxic powers of tobacco smoke from pipe, cigar, and cigarette appeared in the *Lancet* for 6th April 1912.

## Qualitative Tests for Nicotine

Concentrated sulphuric or nitric acid produce no colour change, chlorine water gives a red to brown colour. It is precipitated from solution by iodine in potassium iodide (perceptible in solutions of one part in 250,000), bismuth pot. iodide, mercury pot. iodide, gold, and platinum chlorides. A mixture of concentrated solution of hydrogen peroxide and strong sulphuric acid gives, with nicotine, a dark chocolate-red coloration. If a few drops of a solution of  $\alpha$ -nitroso  $\beta$ -naphthol be evaporated in a porcelain capsule, and a few drops of the base added to the residue, a yellowish-brown tint is obtained. Mercuric chloride gives a white crystalline precipitate with solutions of nicotine, insoluble in water and ether, almost insoluble in alcohol, soluble in dilute hydrochloric or acetic acids. Picric acid added in excess gives a yellow crystalline precipitate even in the presence of foreign organic matter. The picrate,  $B.2C_6H_2(NO_2)_3OH$ , forms short prisms, M.P. 218°C., and is characteristic. With a solution of nicotine 1 in 300,000, and 0.1 per cent. hydrochloric acid, a 5 per cent. solution of potassium silicotungstate produces an immediate turbidity. The delicacy of the test is increased to 1 in a million by increasing the acid to 8 per cent., and allowing several hours for the precipitation.

## The Tobacco Excise Regulation

Tobacco is neither a food nor a drug, so its purity is not guarded by the Food and Drugs Act. It is, however, a very important source of revenue to the State, the present rate of duty being 6s. 5½d. per lb. for "stripped" tobacco (midrib removed), and 6s. 5d. per lb. for whole leaf. An additional duty is charged when



the tobacco contains less than 10 per cent. moisture, and in order that there shall be no loss of revenue due to the admixture of non-dutiable articles, very stringent regulations as to its purity and manufacture are laid down by the Commissioners of Customs and Excise, based upon the authority of Parliament contained in various Finance and Revenue Acts. It must not contain more than 32 per cent. of water, nor more than 4 per cent. of oil. Further, it must not contain any ingredients other than tobacco, water, oil, essential oils (for flavouring), or acetic acid.

With regard to the acetic acid used as a preservative, it is notable that the treatment of tobacco with a small amount of glacial acetic acid in the form of a fine spray is much more effective than the equivalent amount of acid of lower percentage.

### Technical Assay of Tobacco

Chemical analysis of tobacco is not of much assistance in arriving at a decision as to its quality, although it would be much easier to recognise a bad tobacco than a good one by chemical means; for instance, very bad tobacco always contains much protein matter, sulphuric acid, chlorine, and free nicotine, with small portions of amino-nitrogen, potassium salts, etc.; high alkalinity of the ash, on the other hand, indicates good burning qualities, though even this property is usually determined by direct test. As a consequence the only estimations usually made are water, oil, nicotine, inorganic matter, and sand, which, other than nicotine, are required for excise purposes.

**Water.**—A known weight is dried at 100° C. for eight hours. Substances other than water may be vaporised, but, from the wording of the moisture clause of the Revenue Act, these must be calculated as water.

**Oil.**—13.33 gm. of the tobacco, finely cut up, are macerated for twelve hours with 100 c.c. of petroleum ether; 75 c.c. (representing 10 gm. tobacco) of the ethereal extract are rapidly filtered, if necessary, and placed in a tared flask. The ether is distilled off, and the residual extract dried at 100° C. for one hour, and weighed. If the total extract is below 4.5 per cent., it may be assumed that the amount of oil is below 4 per cent. For accurate work the saponification value of the extract would have to be compared with that of the oil used in the manufacture, and even then, as tobacco naturally contains saponifiable substances, disturbing influences are introduced. Determinations of the amount of extractable matter in the unmanufactured leaf might be made, and the result deducted from the amount of extract obtained from the manufactured tobacco, but manufactured tobacco (which has been baked) sometimes gives a lower ether extract than the leaf from which it is made. Amounts varying from 2.9-4.5 per cent. of extractable matter have been obtained by the present writer in two varieties of leaf as imported. *Fesca and Imai* (*J.S.C.I.*, 1888, 759) state that ordinary fat determinations by extracting with ether are useless with tobacco. The method outlined above is, however, the one in use at the Government Laboratory, and this method, or the Soxhlet, is generally followed.

**Inorganic Matter and Sand.**—The tobacco is first dried, and a definite weight incinerated over a small Bunsen flame. After all the "volatile carbon" has been expelled, the incineration is completed in a muffle furnace at a dull red heat, cooled, and the ash moistened with a strong solution of ammonium carbonate to recarbonate the free bases. It is then dried for eighteen hours and weighed as total inorganic matter.

**Sand.**—The ash obtained as above is treated with hydrochloric acid (1 : 6), filtered, the residue dried, ignited, and weighed as sand. Another method is to treat the ash with concentrated hydrochloric acid, evaporate to dryness, heat to 150° C. for half an hour, treat with dilute hydrochloric acid (1 : 12), filter, dry the residue, ignite, and weigh.

**Nicotine.**—Many methods have been proposed for the estimation of nicotine, of varying degrees of reliability. For a comparative study of six methods, see *J. Töth* (*J.S.C.I.*, 1911, 1084). Three methods are here described (for other methods see *Kissling* (*Analyst*, 1904, 378); *J. Töth* (*Analyst*, 1912, 452); *Schröder* (*Analyst*, 1911, 106); *Harrison and Self* (*Pharm. J.*, 1912, 718).

The following method is due to *Garner* (Bulletin No. 102, U.S. Bureau of Plant Industry, Washington, 1907). It is rapid and sufficiently accurate for technical purposes.

Six grams of finely divided air-dried tobacco are well mixed with 3.5 c.c. of a 5 per cent. solution of caustic soda, and transferred to a 250 c.c. stoppered cylinder. Or the tobacco may be mixed in the cylinder by means of a long glass rod. 100 c.c. of petroleum ether are added, and the cylinder vigorously shaken. The mixture is allowed to stand for four hours, the cylinder being laid on its side so as to expose a greater surface of tobacco to the action of the ether, shaking vigorously every half hour. After allowing the mixture to settle, the clear extract is rapidly passed

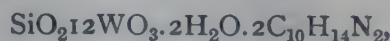


through a filter, 75 c.c. of the filtrate (equal to 4.5 gm. tobacco) being collected. This is allowed to stand in an open flask exposed to the air for half an hour, or air is drawn through it to remove the ammonia, only a small portion of which is extracted by the ether. It is next shaken in a separating funnel with 10 c.c.  $\frac{N}{5}$  sulphuric acid, diluted to 50 c.c. with water. The aqueous layer is drawn off, the petroleum spirit washed twice with a little water, and the excess acid in the aqueous liquid titrated with  $\frac{N}{10}$  alkali, using cochineal as indicator. 1 c.c.  $\frac{N}{5}$  acid is equal to 0.0324 gm. nicotine. The amount of water in the tobacco is determined in a corresponding sample, and the weight taken corrected accordingly. The main difference of the above to Töth's method is that Töth recommends moistening the tobacco and mixing with plaster of paris until the whole forms a dry powdery mass, the plaster of paris retaining the ammonia. Toluene or xylene may be used as the solvent.

**Kissling's Method for the Determination of Nicotine.**—Weigh about 20 gm. of finely-powdered tobacco, which has been previously dried at 60° C., so as to allow it to be powdered into a small beaker. Add 10 c.c. of alcoholic soda solution (6 gm. caustic soda, 40 c.c. water, and 60 c.c. 90 per cent. alcohol) and mix thoroughly. Transfer to a Soxhlet extractor and exhaust for five hours with ether. Evaporate off the ether at a low temperature, and take up the residue with 50 c.c. dilute caustic soda solution (4 gm. caustic soda in 1,000 c.c. of water). Transfer this residue by means of water to a Kjeldahl distillation apparatus, capable of holding about 500 c.c., and distil in a current of steam, using a well-cooled condenser. A few pieces of pumice and a small piece of paraffin should be used to prevent bumping and frothing. Continue the distillation until all the nicotine has passed over, the distillate usually varying from 400 c.c. to 500 c.c. When the distillation is complete only about 15 c.c. of the liquid should remain in the distillation flask. Titrate the distillate with standard sulphuric acid, using phenacetolin or cochineal as indicator. One molecule of sulphuric acid is equivalent to two molecules of nicotine. This is the official method in the United States. *Kissling* (see *Analyst*, 1904, 378) recommended that the tobacco should be mixed with an equal weight of powdered pumice before extraction.

**The Silicotungstate Method for the Determination of Nicotine.**—The method was originally proposed by *Bertram* and *Gavillier*, and has been improved by them and others (see *J.S.C.I.*, 1899, 404; 1909, 326; 1911, 376; *R. Spallino* (*Analyst*, 1914, 43); *H. R. Jensen* (*Pharm. J.*, 1913, 36, 658)). *Jensen* gives the method of preparing silicotungstic acid, its effect on most alkaloids and on many other organic substances.

The tobacco is extracted on the water bath (under a reflex condenser) with ten times its weight of hydrochloric acid (5 per cent.) for fifteen to twenty minutes, the liquid drained off, and the operation repeated four or more times. In the case of tobacco extracts, 5 gm. are diluted to 100 c.c. The nicotine in the liquid is precipitated with silicotungstic acid or its potassium salt. After mixing thoroughly, and allowing to stand eighteen hours (or stirring continuously for one hour if speed is essential), the crystalline precipitate is collected and washed with water, to which has been added a little hydrochloric acid and a few drops of the precipitant. The precipitate is then ignited to the oxides of silica and tungsten,  $\text{WO}_3 \cdot \text{SiO}_2$ . The factor for converting the weight of this into nicotine is 0.1139. The constitution of the compound after drying at 115°-120° C. is stated to be—



but apparently the amount of water present is not sufficiently constant for it to be weighed at this stage.

Instead of igniting the precipitate it may be decomposed with magnesia mixture, distilled in a current of steam, and the nicotine in the distillate titrated as in *Garner's* or *Kissling's* method. Ammonia does not affect the result if less than 2 per cent. be present, and according to *Jensen* not at all by the ignition method.

The present writer has found the silicotungstate method (by ignition) to give high results, which may be due to the fact that the colouring matter extracted by the hydrochloric acid is precipitated by the silicotungstate and the corresponding amount of the oxides left on ignition. The following modification has been adopted: The nicotine is extracted in a Soxhlet as in the *Kissling* method, the ether evaporated off, and the residue taken up with warm dilute hydrochloric acid. After cooling the nicotine is precipitated by silicotungstate, and the precipitate collected, washed, and ignited as in the ordinary method. The fat extracted from the tobacco by the ether does not interfere.



# APPENDIX I

## TABLE I WEIGHTS AND MEASURES

### 1. METRIC SYSTEM

- 1 metre (m.) = 10 decimetres (dm.) = 100 centimetres (cm.) = 1,000 millimetres (mm.)  
= 1.09 yards = 3.281 feet = 39.371 inches.
- 1 litre (l.) = 1,000 cubic centimetres (c.c. or c.cm.) = 0.22 gallon = 1.76 pints = 35.2 fluid oz.
- 1 cubic metre (cb.m.) = 1,000 litres = 220 gallons.
- 1 gramme (g. or gr. or grm.) = 10 decigrammes (dg.) = 100 centigrammes (cg.) = 1,000 milligrammes (mg.) = 15.43 grains.
- 1,000,000 grammes = 1 metric ton; 1,017,960 grammes = 1 ton of 2,240 lbs.
- 1 kilogramme (Kg. or Kilo.) = 1,000 grammes = 35.27 oz. = 2.2 lbs.
- 50 kilogrammes = 1 centner = 1 cwt., nearly.
- 100 kilogrammes = 1 quintal or 1 metric centner = 1 doppelzentner = 1 dz. = about  $\frac{1}{10}$ th ton.
- 1,000 kilogrammes = 1 ton (t.), i.e., *metric ton* = 19 cwt. 77 lbs. = 2204.6 lbs.
- 1 cubic centimetre water = 1 gramme.
- 1 litre water = 1 kilogramme = 2.2 lbs.
- 1 cubic metre water = 1 metric ton = 2204.6 lbs.

### 2. ENGLISH WEIGHTS AND MEASURES

- 1 yard (yd.) = 3 feet = 91.44 centimetres = 0.9144 metre.
- 1 foot (') = 12 inches (") = 30.48 centimetres = 0.3048 metre; 1 cubic foot = 28.315 litres.
- 1 inch = 2.54 centimetres; 1 cubic inch = 0.01639 litre.
- 1 imperial gallon (gal.) = 4 quarts (qts.) = 8 pints (pts.) = 16 gills = 32 noggins = 10 lbs. (of water) = 4.54 litres.
- 1 pint = 0.568 litre = 2 gills = 4 noggins =  $1\frac{1}{4}$  lbs. (water).

In England, by the term gallon (gal.) the Imperial gallon is meant, but in the United States of America the much smaller *apothecary's* or *wine gallon* is understood.

- 1 imperial gallon = 1.2 wine gallons ; 1 wine gallon = 0.8335 imperial gallon.
- 1 wine gallon = 4 quarts = 8 pints = 3.785 litres = 8.35 lbs. water ; 1 litre = 0.264 wine gallon.
- 1 pint (apothecary's measure) = 0.473 litre ; 1 litre = 0.264 pint (apothecary's measure).
- 1 pound avoirdupois (lb.) = 16 oz. = 256 drachms (drm.) = 7,000 grains = 453.6 grams = 0.454 Kilo.
- 1 oz. = 16 drachms = 437.5 grains = 28.35 grams ; 1 fluid oz. = 28.4 c.c.
- 1 hundredweight = 4 quarters (28 lbs. each) = 112 lbs.
- 1 ton (gross ton) = 20 cwt. = 2,240 lbs. = 1,016 Kilos. = 1.016 metric tons.

In England the ton or gross ton of 2,240 lbs. is exclusively used. In the United States of America the term "ton" may mean the gross ton of 2,240 lbs., or the short ton of 2,000 lbs. avoirdupois.

- 1 grain = 0.0648 gram ; 7,000 grains = 1 lb.

TABLE II  
COMPARISON OF THERMOMETERS—CONVERSION OF THERMOMETER DEGREES

- ° C. to ° F. : multiply by 9, divide by 5, then add 32.
- ° F. to ° C. : first subtract 32, then multiply by 5, and divide by 9.

COMPARISON OF CENTIGRADE AND FAHRENHEIT DEGREES

° C.	° F.	° C.	° F.	° C.	° F.	° C.	° F.
+500	+932	+74	+165.2	+45	+113	+16	+60.8
400	752	73	163.4	44	111.2	15	59
300	572	72	161.6	43	109.4	14	57.2
200	392	71	159.8	42	107.6	13	55.4
100	212	70	158	41	105.8	12	53.6
99	210.2	69	156.2	40	104	11	51.8
98	208.4	68	154.4	39	102.2	10	50
97	206.6	67	152.6	38	100.4	9	48.2
96	204.8	66	150.8	37	98.6	8	46.4
95	203	65	149	36	96.8	7	44.6
94	201.2	64	147.2	35	95	6	42.8
93	199.4	63	145.4	34	93.2	5	41
92	197.6	62	143.6	33	91.4	4	39.2
91	195.8	61	141.8	32	89.6	3	37.4
90	194	60	140	31	87.8	2	35.6
89	192.2	59	138.2	30	86	1	33.8
88	190.4	58	136.4	29	84.2	0	32
87	188.6	57	134.6	28	82.4	-1	30.2
86	186.8	56	132.8	27	80.6	2	28.4
85	185	55	131	26	78.8	3	26.6
84	183.2	54	129.2	25	77	4	24.8
83	181.4	53	127.4	24	75.2	5	23
82	179.6	52	125.6	23	73.4	6	21.2
81	177.8	51	123.8	22	71.6	7	19.4
80	176	50	122	21	69.8	8	17.6
79	174.2	49	120.2	20	68	9	15.8
78	172.4	48	118.4	19	66.2	10	14
77	170.6	47	116.6	18	64.4	11	12.2
76	168.8	46	114.8	17	62.6	12	10.4
75	167						



TABLE III

COMPARISON OF HYDROMETER DEGREES TWADDLE AND BAUMÉ WITH THE SPECIFIC GRAVITIES FOR LIQUIDS HEAVIER THAN WATER

Degrees Twaddle.	Degrees Baumé.	Specific Gravity.	Degrees Twaddle.	Degrees Baumé.	Specific Gravity.	Degrees Twaddle.	Degrees Baumé.	Specific Gravity.
1	0.7	1.005	64	35.0	1.320	128	56.3	1.640
2	1.4	1.010	66	35.8	1.330	130	56.9	1.650
4	2.7	1.020	68	36.6	1.340	132	57.4	1.660
6	4.1	1.030	70	37.4	1.350	134	57.9	1.670
8	5.4	1.040	72	38.2	1.360	136	58.4	1.680
10	6.7	1.050	74	39.0	1.370	138	58.9	1.690
12	8.0	1.060	76	39.8	1.380	140	59.5	1.700
14	9.4	1.070	78	40.5	1.390	142	59.9	1.710
16	10.6	1.080	80	41.2	1.400	144	60.4	1.720
18	11.9	1.090	82	42.0	1.410	146	60.9	1.730
20	13.0	1.100	84	42.7	1.420	148	61.4	1.740
22	14.2	1.110	86	43.4	1.430	150	61.8	1.750
24	15.4	1.120	88	44.1	1.440	152	62.3	1.760
26	16.5	1.130	90	44.8	1.450	154	62.8	1.770
28	17.7	1.140	92	45.4	1.460	156	63.2	1.780
30	18.8	1.150	94	46.1	1.470	158	63.7	1.790
32	19.8	1.160	96	46.8	1.480	160	64.2	1.800
34	20.9	1.170	98	47.4	1.490	162	64.6	1.810
36	22.0	1.180	100	48.1	1.500	164	65.0	1.820
38	23.0	1.190	102	48.7	1.510	166	65.5	1.830
40	24.0	1.200	104	49.4	1.520	168	65.9	1.840
42	25.0	1.210	106	50.0	1.530	169	66.1	1.845
44	26.0	1.220	108	50.6	1.540	170	66.3	1.850
46	26.9	1.230	110	51.2	1.550		67	1.872
48	27.9	1.240	112	51.8	1.560		68	1.897
50	28.8	1.250	114	52.4	1.570		69	1.921
52	29.7	1.260	116	53.0	1.580		70	1.946
54	30.6	1.270	118	53.6	1.590		71	1.974
56	31.5	1.280	120	54.1	1.600		72	2.000
58	32.4	1.290	122	54.7	1.610		73	2.031
60	33.3	1.300	124	55.2	1.620		74	2.059
62	34.2	1.310	126	55.8	1.630			

*Note.*—The degrees in Twaddle’s hydrometer bear a direct relationship to the specific gravity and may be obtained from the same by the following formula in which *d* represents the specific gravity and *n* the number of degrees Twaddle:  $n = \frac{1000\ d - 1000}{5}$ . On the other hand by the

formula  $d = \frac{5n + 1000}{1000}$  the degrees Twaddle are converted into the corresponding specific gravity.

For values below 2.0 the degrees Twaddle may also be obtained from the specific gravity by moving the decimal point two figures to the right, striking off the first figure and multiplying the rest by 2, as per the following example:—

Specific gravity 1.133 :  
113.3 :  
13.3 × 2 :  
26.6° Twaddle.

TABLE IV

DENSITIES CORRESPONDING TO BAUMÉ'S HYDROMETER FOR LIQUIDS  
LIGHTER THAN WATER (*Francaur*)

° B.	Density.	° B.	Density.	° B.	Density.	° B.	Density.
10	1.000	23	0.918	36	0.849	49	0.789
11	0.993	24	0.913	37	0.844	50	0.785
12	0.986	25	0.907	38	0.839	51	0.781
13	0.980	26	0.901	39	0.834	52	0.777
14	0.973	27	0.896	40	0.830	53	0.773
15	0.967	28	0.890	41	0.825	54	0.768
16	0.960	29	0.885	42	0.820	55	0.764
17	0.954	30	0.880	43	0.816	56	0.760
18	0.948	31	0.874	44	0.811	57	0.757
19	0.942	32	0.869	45	0.807	58	0.753
20	0.936	33	0.864	46	0.802	59	0.749
21	0.930	34	0.859	47	0.798	60	0.745
22	0.924	35	0.854	48	0.794		



## APPENDIX II

INDEX LIST OF TRADE NAMES OF SYNTHETIC DRUGS,  
PHOTOGRAPHIC DEVELOPERS, ETC.

NOTE: *Many of these are Registered Trade Names, the property of the manufacturers. For newer trade names, see page 685.*

- Abanone.**—Magnesium phosphotartrate.
- Acetomorphine.**—Diacetylmorphine,  
 $C_{17}H_{17}NO_3(C_2H_5O)_2$ .
- Acetopyrin.**—Antipyrine acetylsalicylate,  
 $C_{11}H_{12}N_2O, C_2H_5O, OC_6H_4, COOH$ .
- Acetosal.**—Acetylsalicylic acid,  
 $C_2H_3O, OC_6H_4, CO_2H$ .
- Acetozone.**—Mixture of equal parts of acetylbenzoyl peroxide,  $C_6H_5CO, O, O, C_2H_5O$ , and kieselguhr.
- Acetysal.** See acetosal.
- Acidol.**—Betaine hydrochloride,  $C_5H_{11}NO_2, HCl$ .
- Acitrin.**—2-Phenylquinoline-4-carboxylic acid ethyl ester,  $C_9H_5N(C_6H_5)CO_2C_2H_5$ .
- Acopyrin.** See acetopyrin.
- Adalin.**—Bromodiethylacetylurea,  
 $(C_2H_5)_2CBr, CO, NH, CO, NH_2$ .
- Adamon.**—Dibromodihydrocinnamic acid bornyl ester,  $C_6H_5(CHBr)_2CO_2C_{10}H_{17}$ .
- Adigan.**—Digitalis preparation containing all the active principles except digitonin, this having been removed by precipitation with cholesterol in alcoholic solution.
- Adrenal.**—Crystalline base from the suprarenal gland.
- Adrenaline.**—*o*-Dihydroxyphenylmethylaminomethylcarbinol hydrochloride,  
 $(HO)_2C_6H_3, CH(OH), CH_2, NH(CH_3), HCl$ .
- Adreucaine.** See eudrenine.
- Afridol.**—Sodium salt of hydroxymercury-*o*-toluic acid,  $CH_3, C_6H_3(CO_2Na)HgOH$ .
- Agnin.**—Adeps lanæ or purified wool fat.
- Agnolin.** See agnin.
- Agobillin.**—Strontium cholate mixed with small quantities of strontium salicylate and diacetylphenolphthalein.
- Agurin.**—Addition product of theobromine-sodium and sodium acetate,  $C_7H_7N_4O_2Na, C_2H_3O_2Na$ .
- Albargin.**—Gelatin-silver (15 % Ag).
- Aldoform.**—A formaldehyde preparation.
- Aleudrin.**—Carbamic acid ester of *aa*-dichloroisopropyl alcohol,  $(CH_2Cl)_2, CH, O, CO, NH_2$ .
- Alformin.**—16 % solution of basic aluminium formate,  $Al_2(OH)_2(HCO_2)_4$ .
- Alginoid iron.** See algiron.
- Algiron.**—Iron compound of alginic acid (from seaweed); contains 11 % Fe.
- Allmatein.**—Condensation product of hæmatoxylin and formaldehyde,  $CH_2O_2(C_{16}H_{12}O_5)_2 : CH_2$ .
- Allosan.**—Santalyl allophanate,  
 $NH_2, CO, NH, CO_2, C_{15}H_{23}$ .
- Alphogen.**—Succinyl peroxide,  
 $(COOH, CH_2, CH_2, CO)_2O_2$ .
- Alphozone.** See alphogen.
- Althein.**—Asparagin,  
 $C_2H_3(NH_2)(CO_2H)CO, NH_2 + H_2O$ .
- Alypin.**—Benzoyl-1, 3-tetramethyldiaminoethyl 2 isopropyl alcohol hydrochloride,  
 $C_6H_5CO, O(C_2H_5)C[CH_2, N(CH_3)_2]_2, HCl$ .
- Amarin.**—Triphenyldihydroglyoxaline,  
 $C_6H_5, C, NH > CH, C_6H_5$ ,  
 $C_6H_5, C, NH >$ .
- Amenyl.**—Methylhydrastimide hydrochloride,  
 $CH_2O_2 : C_6H_2(CO)_2N(CH_3), HCl$ .
- Amidopyrin.**—Dimethylaminoantipyrine,  
 $C_{11}H_{11}N_2O, N(CH_3)_2$ .
- Amphotropin.**—Hexamethylenetetramine camphorate,  $(C_6H_{12}N_4)_2, C_8H_{14}(COOH)_2$ .
- Amylarine.**—Isoamyltrimethylammonium hydroxide,  $C_5H_{11}(CH_3)_3N, OH$ .
- Anæsthesin.**—Ethyl ester of *p*-aminobenzoic acid,  
 $NH_2, C_6H_4, CO_2C_2H_5$ .
- Anæsthone.** See anæsthesin.
- Analutos.** See kalmopyrin.
- Angioneurosin.**—Nitroglycerin,  $C_3H_5(O, NO_2)_3$ .
- Anisothobromine.**—Addition product of theobromine-sodium and sodium anisate,  
 $C_7H_7N_4O_2Na, C_6H_4(OCH_3)CO_2Na$ .
- Anogon.**—Mercury salt of 2,6-di-iodophenol-4-sulphonic acid,  $C_6H_2I_2(OHg)(SO_3Hg)$ .
- Antacedin.**—Calcium saccharate.
- Anthrasol.**—Coal tar distillate having colour and consistence of olive oil.
- Antiarthrin.**—Condensation product of saligenin and tannin, probably the hydroxybenzyl ester of tannic acid.
- Antileprol.**—Purified chaulmoogra oil.
- Antiluetin.**—Potassium-ammonium antimonyltartrate,  $[SbO(C_4H_4O_6)_2KNH_4]_2H_2O$ .
- Antiperiostin.**—Mercury iodocantharidate,  
 $C_8H_{11}IO(COO)_2Hg$ .
- Antipyoninum.**—“Neutral” sodium tetraborate, prepared by fusing together borax and boric acid.
- Antisclerosine.**—Mixed inorganic salts of normal blood.



**Antodin.**—Phenyl ether of glycerol,  
 $C_3H_5(OH)_2O.C_6H_5$ .

**Aperitol.**—Mixture of equal parts of isovaleryl-  
 and acetyl-phenolphthalein.

**Aponal.**—Amyl carbamate,  $NH_2.COOC_5H_{11}$ .

**Appallagin.**—Mercury compound of nosophen  
 (tetraiodophenolphthalein).

**Apyron.**—Lithium acetylsalicylate,  
 $C_2H_3O.OC_6H_4.CO_2Li$ .

**Archibromin.**—Monobromoisovaleryl glycolylurea.  
 $CH_2(OH).CO.NH.CO.NH.CO.C_4H_8Br$ .

**Archiodin.**—Monoiodoisovaleryl glycolylurea.

**Argaldin.**—Combination of albumin-silver and  
 hexamethylenetetramine (10 % Ag).

**Argoferment.**—Colloidal silver.

**Argyrol.**—Silver-vitellin (20-30 % Ag).

**Argulan.**—Mercury compound of dimethylphenyl-  
 pyrazolonesulphamine,  
 $C_{11}H_{11}N_2O.NH.SO_3HgOH$ .

**Arheol.**—Santalol,  $C_{15}H_{24}O$ .

**Arhoïn.**—Addition product of diphenylamine and  
 ethylthymyl-benzoate,  
 $(C_6H_5)_2NH.C_{10}H_{13}.C_6H_4.CO_2C_2H_5$ .

**Aristochin.** See aristochinine.

**Aristochinine.**—Carbonic ester of quinine,  
 $CO(OC_{20}H_{23}N_2O)_2$ .

**Arrhenal.**—Sodium methylarsinate,  
 $AsO(CH_3)(ONa)_2.6H_2O$ .

**Arsacetin.**—Sodium *p*-acetylaminophenylarsinate,  
 $C_2H_3O.NH.C_6H_4.AsO(ONa)(OH).3-4H_2O$ .

**Arsacetin-quinine.**—Contains 43 % of arsacetin  
 and 54 % of quinine.

**Arsalyt.**—Bismethylaminotetra-aminoarsenoben-  
 zene.

**Arsamin.** See atoxyl.

**Arsan.**—Glidin preparation containing silver.

**Arsanilic Acid.**—*p*-Aminophenylarsinic acid,  
 $NH_2.C_6H_4.AsO(OH)_2$ .

**Arsen-phenol-amine.** See salvarsan.

**Arterenol.**—*o*-Dihydroxyphenylaminomethylcar-  
 binol hydrochloride,  
 $(HO)_2C_6H_3.CH(OH).CH_2NH_2.HCl$ .

**Asiphyl.** See asyphil.

**Aspirin, Soluble.** See kalmopyrin.

**Aspirophen.**—Aminoacetphenetidide acetylsalicy-  
 late,  
 $C_2H_5O.C_6H_4.NH.C_2H_2O.NH_2$ ,  
 $C_2H_3O.OC_6H_4.COOH$ .

**Asquirrol.**—Mercury dimethoxide,  $(CH_3O)_2Hg$ .

**Astrolin.**—Antipyrine methyl-ethyl-glycollate.

**Asurol.**—Addition product of mercury salicylate  
 and sodium aminohydroxy-isobutyrate.

**Asyphil.**—Mercury salt of atoxyl,  
 $(NH_2C_6H_4.AsO.(OH)O)_2Hg$ .

**Atophan.**—2-Phenylquinoline-4-carboxylic acid,  
 $C_9H_5N(C_6H_5)COOH$ .

**Atoxyl.**—Sodium *p*-aminophenylarsinate,  
 $NH_2.C_6H_4.AsO(OH)(ONa).xH_2O$ .

**Atrinal.**—Atropinesulphuric acid,  $C_{17}H_{25}O_6NS$ .

**Atyrosyl.** See asyphil.

**Azovernin.**—Acetylaminoozotoluene,  
 $CH_3.C_6H_4.N_2.C_6H_3(CH_3).NH.C_2H_5O$ .

**Barbitone.** See veronal.

**Barutin.**—Addition product of theobromine-  
 barium and sodium salicylate.

**Benzinoform.**—Carbon tetrachloride.

**Benzosalin.**—Methyl benzoyl salicylate,  
 $C_6H_4(O.CO.C_6H_5)COOCH_3$ .

**Biogen.**—Magnesium peroxide.

**Biolactyl.**—Preparation of lactic acid bacilli.

**Bisciniod.**—Combination of cinchonidine hydro-  
 dide and bismuth iodide,  $C_{19}H_{22}N_2O, HI, BiI_3$ .

**Bismon.**—Colloidal bismuth.

**Bismutose.**—Contains about 22 % Bi and 66 %  
 albumin.

**Blankit.**—Sodium hydrosulphite.

**Blenal.**—Carbonic acid ester of santalol,  
 $CO(OC_{15}H_{23})_2$ .

**Bornyval.**—Bornyl isovalerate,  
 $C_4H_9CO.O.C_{19}H_{17}$ .

**Bornyval, New.**—Bornyl isovaleryl glycollate,  
 $C_4H_9COOCH_2.COOC_{10}H_{17}$ .

**Boroform.**—Solution of formaldehyde in sodium  
 glyceroborate.

**Borsalyl.**—Sodium borosalicylate.

**Borovertin.**—Hexamethylenetetramine triborate,  
 $C_6H_{12}N_4.3HBO_2$ .

**Bromeigon.**—Albumin preparation containing bro-  
 mine.

**Bromelia, cryst.**— $\beta$ -Naphthyl ethyl ether,  
 $C_{10}H_7.O.C_2H_5$ .

**Brometone.**—Tribromo tertiary butyl alcohol,  
 $CBr_3.C(CH_3)_2OH$ .

**Brominol.**—Brominated sesamé oil (33 % Br).

**Brominoleum.** See brominol.

**Bromochinol.**—Acid dibromosalicylate of quinine,  
 $C_{20}H_{24}N_2O_2.2C_6H_2Br_2(OH)COOH$ .

**Bromoglidin.**—Wheat gluten preparation contain-  
 ing 10 % Br.

**Bromogluten.**—Vegetable albumin preparation  
 containing 8 % Br.

**Bromolein.**—Brominated unsaturated fatty acids  
 of almond oil (20 % Br).

**Bromoprotein.** See bromogluten.

**Bromotan.**—Bromotannin-methylene-urea.

**Bromural.**— $\alpha$ -Bromoisovalerylurea,  
 $C_4H_8Br.CO.NH.CO.NH_2$ .

**Brophenin.**—Bromoisovalerylphenocoll; a bromi-  
 nated phenetidine derivative.

**Brovalol.**—Bornyl bromovalerate,  
 $C_4H_8Br.COO.C_{10}H_{17}$ .

**Bynin.**—Liquid malt extract.

**Cacodyliagol.**—Guaiacol cacodylate,  
 $(CH_3)_2AsO.O.C_6H_4(OCH_3)_2.H_2O$ .

**Cajuputol.**—Cineol (eucalyptol),  $C_{10}H_{18}O$ .

**Calcidine.**—Calcium iodide.

**Calcinol.**—Calcium iodate.

**Calculusol.**—Effervescent preparation of potassium  
 bicarbonate and piperidine-*p*-sulphamine ben-  
 zoate,  $SO_2(NH_2)C_6H_4COOH, C_8H_{11}N$ .

**Calomelol.**—Colloidal calomel.

**Camphoid.**—Collodion substitute; 1 part of  
 pyroxylin in 20 parts each of camphor and  
 absolute alcohol, by weight.

**Camphoral.**—Camphoric acid ester of santalol,  
 $C_8H_{14}(COO)_2(C_{15}H_{23})_2$ .

**Camphosan.**—Solution of 15 parts of camphoric  
 acid methyl ester in 85 parts of santalol.

**Canadol.**—Light petroleum spirit,  
 sp. gr. 0.650-0.700.

**Casumen.**—Soluble form of casein ("flocculent  
 casein"); contains 90 % of protein.

**Celloidin.**—Pyroxylin purified by solution in alco-  
 hol and ether.

**Cellotropin.**—Benzoic ester of arbutin,  
 $C_6H_4OC_6H_{11}O_5.O.COC_6H_5$ .

**Ceredine.**—Special dry powdered yeast.

**Cerolin.**—Solid extract of yeast, containing fat.

**Cetiacol.**—Pyrocatechol methyl cetyl ether,  
 $C_8H_4(OCH_3)(OC_{16}H_{33})$ .



**Chinaphenin.** See quinaphenin.  
**Chinaphthol.** See quinaphthol.  
**Chineonal.** See quineonal.  
**Chininum lygosinatum.** See quinine lygosinate.  
**Chinoform.** See quinoform.  
**Chinosol.** See quinosol.  
**Chloralamid.**—Chloral formamide,  
 $\text{CCl}_3 \cdot \text{CH}(\text{OH}) \cdot \text{CO} \cdot \text{NH}_2$ .  
**Chloretone.**—Trichloro tertiary butyl alcohol,  
 $\text{CCl}_3 \cdot (\text{CH}_3)_2 \text{C} \cdot \text{OH} \cdot \frac{1}{2} \text{H}_2\text{O}$ .  
**Chlorin.**—Dinitroresorcinol,  
 $(\text{NOH})\text{O} : \text{C}_6\text{H}_2 : \text{O}(\text{NOH})$ .  
**Chlorobrom.**—A solution of potassium bromide 6,  
 chloral formamide 6, and water 58 parts.  
**Chloryl anaesthetic.**—Ethyl chloride.  
**Chromoform.**—Combination of methylhexamethy-  
 lenetetramine and dichromic acid,  
 $(\text{C}_6\text{H}_{12}\text{N}_4\text{CH}_3)_2\text{Cr}_2\text{O}_7$ .  
**Chrysoform.**—Dibromodi-iodohexamethylene-  
 tetramine,  $\text{C}_6\text{H}_8\text{Br}_2\text{I}_2\text{N}_4$ .  
**Cibrola.**—Preparation of milk and glycerophos-  
 phates.  
**Cicatricine.**—A solution containing thiosinamine  
 20, antipyrine 33, and eucaine lactate 0.65  
 part per 100.  
**Citarin.**—Sodium anhydromethylenecitrate,  
 $\text{O} \begin{array}{c} \text{CH}_2 \\ \diagup \quad \diagdown \\ \text{CO} \end{array} \text{CO} \begin{array}{c} \text{CH}_2 \cdot \text{COONa} \\ \diagdown \quad \diagup \\ \text{CH}_2 \cdot \text{COONa} \end{array}$   
**Citrocoll.**—Neutral aminophenacetin citrate.  
**Cocaethylin.**—Ethyl ester of benzoyllecgonine,  
 $\text{C}_6\text{H}_5\text{CO} \cdot \text{C}_8\text{H}_{13}\text{NO} \cdot \text{COOC}_2\text{H}_5$ .  
**Codeonal.**—Mixture of 1 part of medinal and 2 of  
 codeine-veronal.  
**Colalin.**—Cholalic acid,  $\text{C}_{24}\text{H}_{40}\text{O}_5 \cdot \text{H}_2\text{O}$ .  
**Corylin.**—Menthyl ethyl glycollate,  
 $\text{CH}_2\text{O}(\text{C}_{10}\text{H}_{19}) \cdot \text{COOC}_2\text{H}_5$ .  
**Corpyrin.** See acetosal.  
**Cresgol.**—Mercury-potassium salt of cresolsul-  
 phonic acid.  
**Cresosteril.**—Acid ortho-oxalic ester of *m*-cresol,  
 $\text{CH}_3 \cdot \text{C}_6\text{H}_4 \cdot \text{O} \cdot \text{C}(\text{OH})_2 \cdot \text{C}(\text{OH})_2 \cdot \text{OC}_6\text{H}_4(\text{CH}_3)$ .  
**Cryogenin.**—*m*-Benzaminosemicarbazide,  
 $\text{NH}_2 \cdot \text{CO} \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{NH} \cdot \text{CO} \cdot \text{NH}_2$ .  
**Cupferron.**—Ammonium compound of nitroso-  
 phenyl-hydroxylamine.  
**Cupratin.**—Copper albuminate.  
**Cupri-aseptol.**—Copper *m*-phenolsulphonate,  
 $(\text{HO} \cdot \text{C}_6\text{H}_4 \cdot \text{SO}_3)_2\text{Cu}$ .  
**Cupricin.**—Cuprous cyanide.  
**Cuprocitrol.**—Copper citrate,  $2\text{Cu}_2\text{C}_6\text{H}_4\text{O}_7 \cdot 5\text{H}_2\text{O}$ .  
**Cuprol.**—Compound of nucleic acid and copper.  
**Cusylol.**—Soluble copper citrate.  
**Cycloform.**—Isobutyl ester of *p*-aminobenzoic acid,  
 $\text{C}_6\text{H}_4(\text{NH}_2)\text{COOC}_4\text{H}_9$ .  
**Cypridol.**—Mercuric iodide (1 %) in sterilised oil.  
**Cystamin.** See hexamine.  
**Cystogen.** See hexamine.  
**Cystopurin.**—Addition product of hexamethylene-  
 tetramine and sodium acetate,  
 $\text{C}_6\text{H}_{12}\text{N}_4 \cdot 2\text{C}_2\text{H}_3\text{O}_2\text{Na} \cdot 6\text{H}_2\text{O}$ .  
**Deba.** See veronal.  
**Dentalone.**—Solution of chloretone in essential  
 oils.  
**Dermogen.** See ektogen.  
**Desalgin.**—“Colloidal chloroform”; an albumin-  
 ous substance combined with about 25 %  
 $\text{CHCl}_3$ .  
**Dial-Ciba.**—Diallylbarbituric acid,  
 $(\text{C}_2\text{H}_5)_2\text{C} \begin{array}{c} \text{CO} \cdot \text{NH} \\ \diagup \quad \diagdown \\ \text{CO} \cdot \text{NH} \end{array} \text{CO}$ .

**Diaspirin.**—Succinylsalicylic acid,  
 $(\text{CH}_2 \cdot \text{COO})_2(\text{C}_6\text{H}_4\text{COOH})_2$ .  
**Digipotene.**—Preparation containing the whole of  
 the glucosides of digitalis leaves.  
**Dioform.**—Acetylene dichloride,  $\text{CHCl} : \text{CHCl}$ .  
**Diogen.**—Sodium salt of aminonaphtholdisulphonic  
 acid,  $\text{NH}_2 \cdot \text{C}_{10}\text{H}_4(\text{OH})(\text{SO}_3\text{Na})_2$ .  
**Diogenal.**—Dibromopropyldiethylbarbituric acid,  
 $(\text{C}_2\text{H}_5)_2\text{C} \begin{array}{c} \text{CO} \cdot \text{N}(\text{C}_2\text{H}_5\text{Br}_2) \\ \diagup \quad \diagdown \\ \text{CO} \quad \text{NH} \end{array} \text{CO}$ .  
**Dioxogen.**—A 30 % solution of hydrogen peroxide.  
**Diplosal.**—Salicylosalicylic acid,  
 $\text{HO} \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{O} \cdot \text{C}_6\text{H}_4 \cdot \text{COOH}$ .  
**Dipropoesin.**—Urea derivative containing the resi-  
 dues of 2 mols. of propæsin,  
 $\text{CO}(\text{NH} \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{C}_3\text{H}_7)_2$ .  
**Disalol.**—Phenyl salicylosalicylate,  
 $\text{HO} \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{O} \cdot \text{C}_6\text{H}_4 \cdot \text{COOC}_6\text{H}_5$ .  
**Dispermin.**—Piperazine,  $\text{NH} \begin{array}{c} \text{CH}_2 \cdot \text{CH}_2 \\ \diagup \quad \diagdown \\ \text{CH}_2 \cdot \text{CH}_2 \end{array} \text{NH}$ .  
**Durine.**—A formalin preparation.  
**Dymal.**—Didymium salicylate.  
**Edinol.**—*m*-Amino-*o*-hydroxybenzylalcohol hydro-  
 chloride,  $\text{HO} \cdot \text{C}_6\text{H}_3(\text{NH}_2)\text{CH}_2\text{OH} \cdot \text{HCl}$ .  
**Ehrlich-Hata “606.”** See salvarsan.  
**Ektogen.**—Zinc peroxide.  
**Elarson.**—Strontium salt of chloroarsenobehenolic  
 acid (13 % As.).  
**Elbon.**—Cinnamoyl-*p*-hydroxyphenylurea.  
**Electrargol.**—Electrolytic colloidal silver.  
**Embarin.**—Sodium mercurisalicylsulphonate.  
**Empyroform.**—Condensation product of tar and  
 formaldehyde.  
**Enesol.**—Mercury salicylarsenate (38 % Hg).  
**Epineine.**—3,4-Dihydroxyphenylethylmethyla-  
 mine,  $(\text{HO})_2\text{C}_6\text{H}_3 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{NH} \cdot \text{CH}_3$ .  
**Epinephrine.**—*o*-Dihydroxy-4-methylamino-*e*-  
 thanolbenzene,  
 $(\text{HO})_2\text{C}_6\text{H}_3 \cdot \text{CH}(\text{OH}) \cdot \text{CH}_2 \cdot \text{NH} \cdot \text{CH}_3$ .  
**Epiosine.**—1-Methyl-4,5-diphenyleneimidazole,  
 $\begin{array}{c} \text{C}_6\text{H}_4 - \text{C} \cdot \text{N}(\text{CH}_3) \\ | \quad \parallel \\ \text{C}_6\text{H}_4 - \text{C} - \text{N} = \text{CH} \end{array}$ .  
**Epirenan.** See adrenaline.  
**Erepton.**—Meat preparation in which proteins are  
 completely resolved into amino-acids.  
**Ericin.** See mesotan.  
**Ervasin.**—Acetylcresotinic acid.  
**Escalin.**—Aluminium powder mixed to a paste  
 with glycerin.  
**Estoral.**—Menthyl borate,  $\text{B}(\text{O} \cdot \text{C}_{10}\text{H}_{19})_3$ .  
**Euboruy.**— $\alpha$ -Bromoisovaleric ester of borneol,  
 $\text{C}_4\text{H}_8\text{Br} \cdot \text{COOC}_{10}\text{H}_{17}$ .  
**Eucodeine.**—Codeine methyl bromide,  
 $\text{C}_{18}\text{H}_{21}\text{NO}_3 \cdot \text{CH}_3\text{Br}$ .  
**Eucol.**—Guaiacol acetate,  $\text{CH}_3\text{O} \cdot \text{C}_6\text{H}_4 \cdot \text{O} \cdot \text{C}_2\text{H}_5$ .  
**Eudrenine.**—A solution containing 0.01 grm. of  
 eucaine and 0.03 mgrm. of adrenaline per c.c.  
**Euguform.**—Acetylated guaiacalform (condensation  
 product of guaiacol and formaldehyde).  
**Eulatin.**—Mixture of *p*-bromobenzoic acid,  
*o*-aminobenzoic acid, and antipyrine.  
**Eumydrine.**—Methylatropine nitrate,  
 $\text{C}_{16}\text{H}_{20}\text{NO}_3(\text{CH}_3)_2\text{NO}_3$ .  
**Euphyllin.**—Mixture of equal proportions of  
 primary and secondary theophylline-ethylene-  
 diamine,  
 $\text{C}_2\text{H}_4(\text{NH}_2)_2 \cdot \text{C}_7\text{H}_8\text{N}_4\text{O}_2 + \text{C}_2\text{H}_4(\text{NH}_2)_2 \cdot 2\text{C}_7\text{H}_8\text{N}_4\text{O}_2$ .  
**Eupnine.**—Caffeine preparation containing iodine.  
**Euporphine.**—Apomorphine methyl bromide,  
 $\text{C}_{17}\text{H}_{17}\text{NO}_2 \cdot \text{CH}_3\text{Br} \cdot \text{H}_2\text{O}$ .



**Eupyrine.**—*p*-Phenetidine-vanillin ethyl carbonate,  
 $C_6H_4(OC_2H_5)N:CH.C_6H_3(OCH_3)O.CO_2C_2H_5$ .

**Euresol.**—Resorcinol monoacetate,  
 $C_6H_5(OH)(O.C_2H_5O)$ .

**Euquinine.**—Quinine ethyl carbonate,  
 $C_2H_5O.CO.OC_{20}H_{23}N_2O$ .

**Euscopol.**—Inactive scopolamine hydrobromide,  
 $C_{17}H_{21}NO_4.HBr$ .

**Eustenine.**—Addition product of theobromine-sodium and sodium-iodide,  
 $C_7H_7N_4O_2Na.NaI$ .

**Exodin.**—Mixture of diacetylrufigallic acid tetramethyl ether 23, rufigallic hexamethyl ether 30, and acetylrufigallic pentamethyl ether 47 %.

**Fæxin.** See ceredine.

**Fermenlactyl.**—Preparation of lactic acid bacilli.

**Feronuclin.**—Dry yeast extract.

**Ferratogen.** See ferrinol.

**Ferrichthol.**—Ichthyol preparation containing iron.

**Ferrinol.**—Iron nucleinate; contains 21 %  $Fe_2O_3$  and 2½ % P.

**Fibrolysin.**—15 % solution of a combination of thiosinamine (2 mols.) and sodium salicylate (1 mol.).

**Fluoram.**—Ammonium bifluoride.

**Forgenin.**—Tetramethyl-ammonium formate,  
 $H.COON(CH_2)_4$ .

**Formamint.**—Preparation obtained from 1 mol. of lactose and at least 5 mols. of formaldehyde.

**Forman.**—Chloromethyl menthyl ether,  
 $C_{10}H_{19}O.CH_2Cl$ .

**Formicin.**—Formaldehyde-acetamide,  
 $CH_3.CO.NH.CH_2OH$  or  
 $CH_3.C(:NH).O.CH_2OH$ .

**Formidin.**—Methylenedisalicylic iodide,  
 $C_{15}H_{16}O_6I_2$ .

**Formitrol.**—Formaldehyde preparation.

**Formolyptol.** See formitrol.

**Formurol.**—Addition product of hexamethylene-tetramine and sodium citrate,  
 $C_6H_{12}N_4.C_6H_7O_7Na$ .

**Fredo.**—Calcium hydrosulphite.

**Furfurin.**—A glyoxaline derivative,  
 $C_3H_3N_2(C_4H_3O)_3$ .

**Gadnol.**—Extract containing the alcohol-soluble constituents of cod-liver oil.

**Gallogen.**—Ellagic acid,  $C_{14}H_6O_8$ .

**Gastrosan.**—Bi-smuth basilicylate.

**Gaultheriasalol.**—Methyl salicylosalicylate,  
 $HO.C_6H_4.CO.OC_6H_4.COOCH_3$ .

**Glidine.**—A protein preparation from wheat.

**Glonoin.**—Nitroglycerin.

**Glycarbin.**—Glyceryl carbonate.

**Glycerin-formal.**—A condensation product of formaldehyde and glycerol,  $O.CH_2.O$ .  
 $CH_2OH.CH—CH_2$ .

**Glycobrom.**—Glyceryl ester of dibromohydrocin-namic acid,  $C_3H_5[O.CO.(CHBr)_2C_6H_5]_3$ .

**Glycocyammine.**—Guanidine acetic acid.

**Glycosal.**—Monosalicylic ester of glycerol,  
 $C_3H_5(OH)_2.O.CO.C_6H_4(OH)$ .

**Gomaine.**—Solution of iodoform and camphor in sesamé oil.

**Griserin, Novum.**—Iodohydroxyquinoline sulphonic acid,  
 $C_9H_7I(OH)(SO_3H)N$ , mixed with  
 20 %  $NaHCO_3$ .

**Gualachinol.**—Quinine dibromoguaiacolate,  
 $C_6H_2Br_2(OCH_3)OH.C_{20}H_{24}N_2O_2$ .

**Gualamaltin.**—Mixture of malt extract and potassium sulphoguaiacolate.

**Guatannin.**—Guaiacol tannocinnamate.

**Gynoval.**—Isobornyl isovalerate,  
 $C_4H_9.COOC_{10}H_{17}$ .

**Hectine.**—Sodium benzosulpho-*p*-aminophenylarsinate,  
 $C_6H_5.SO_2NH.C_6H_4.AsO(OH)(ONa)$ .

**Hediorite.**—Lactone of  $\alpha$ -glucoheptonic acid.

**Hegonon.**—Ammonio-silver nitrate-albumose (7 % Ag).

**Helcosol.**—Basic bismuth pyrogallate,  
 $HO.C_6H_3O_2BiOH$ .

**Helicon.** See acetosal.

**Helmitol.**—Hexamethylenetetramine anhydromethylenecitrate,  $C_6H_{12}N_4.C_7H_6O_7$ .

**Hemisine.** See adrenaline.

**Hermophenyl.**—Mercury sodium phenoldisulphonate,  $(SO_3Na)_2C_6H_2O(Hg)$ .

**Hetoform.**—Basic bismuth cinnamate,  
 $(C_6H_5.CH:CH.CO_2)_3Bi.Bi_2O_3$ .

**Hetralin.**—Addition product of resorcinol and hexamethylenetetramine,  
 $C_6H_{12}N_4.C_6H_4(OH)_2$ .

**Hexal.**—Hexamethylenetetramine salicylsulphonic acid,  $C_6H_{12}N_4.(HO)C_6H_3(COOH)SO_3H$ .

**Hexamine.**—Hexamethylenetetramine,  $C_6H_{12}N_4$ .

**Hexanatrín.**—Combination of hexamethylene-tetramine and acid sodium phosphate.

**Hexanitrin.**—Mannitol hexanitrate,—  
 $CH_2O(NO_2)(CHO.NO_2)_4.CH_2ONO_2$ .

**Histamin.**— $\beta$ -Iminazolyethylamine.

**Homorenon.**—Ethylaminoacetopyrocatechol hydrochloride,  
 $(HO)_2.C_6H_3.CO.CH_2.NH(C_2H_5).HCl$ .

**Hopogan.** See magnesium perhydrol.

**Hydramin.**—A combination of *p*-phenylenediamine and quinol.

**Hydrargol.**—Mercury succinimide,  
 $[C_2H_4(CO)_2N]_2Hg$ .

**Hydrargotin.**—Mercury tannate (50 % Hg).

**Hydrarsan.**—Solution of a mixture of arsenious mercuric, and potassium iodides and antipyrine.

**Hydriodol.** See cypridol.

**Hydropyrin.** See apyrin.

**Hydrosulphite N.F.**—Condensation product of formaldehyde and sodium hydrosulphite; mixture of formaldehyde sodium bisulphite  $NaHSO_3$ ,  $CH_2O$ , and formaldehyde-sodium sulphonylate,  $NaHSO_2$ ,  $CH_2O$ .

**Hydrosulphite N.F. extra, or conc., or extra conc.**—Formaldehyde-sodium-sulphonylate.

**Hyperol.**—Compound of hydrogen peroxide and urea, with a trace of citric acid to render stable.

**Hypnogen.** See veronal.

**Hydraldite A.** See hydrosulphite N.F.

**Hydraldite C.** See hydrosulphite N.F. extra.

**Iachiol.**—Silver fluoride.

**Ichthargan.**—Silver ichthyolsulphonate (30 % Ag).

**Ichthermol.**—Mercury compound of ichthyol.

**Ichthosulphol.**—Ichthyol.

**Ichthynal.** See ichthosulphol.

**Ichthyolidin.**—Piperazine ichthyolate.

**Ichthyol-salicyl.**—Mixture of ichthyol and sodium salicylate.



- Imogen.**—Sodium diamidonaphtholsulphonate,  $(\text{NH}_2)_2\text{C}_{10}\text{H}_5(\text{OH})\text{SO}_3\text{Na}$ .
- Indoform.**—Salicylic methylene acetate; from formaldehyde and acetylsalicylic acid.
- Insipin.**—Diglycollic ester of quinine sulphate,  $(\text{CH}_2\text{COO}.\text{C}_{20}\text{H}_{23}\text{N}_2\text{O})_2\text{O}.\text{H}_2\text{SO}_4.3\text{H}_2\text{O}$ .
- Iodanytol.**—10% solution of iodine in anytin (a 33% solution of ichthyol).
- Iodelgon.**—Albumin preparation containing iodine.
- Iodin.**—Iodised arachis oil.
- Iodinol.**—Iodised sesamé oil.
- Iodival.**—Monoiodoisovalerylurea,  $(\text{CH}_3)_2\text{CH}.\text{CH}.\text{CO}.\text{NH}.\text{CO}.\text{NH}_2$ .
- Iodocol.**—Prepared from guaiacol and iodine in sodium iodine.
- Iodofan.**—Monoiododihydroxybenzene - formaldehyde.
- Iodoglidine.**—Preparation of wheat gluten containing 10% I.
- Iodoglobin.**—Di-iodotyrosine,  $\text{HO}.\text{C}_6\text{H}_2\text{I}_2.\text{CH}_2.\text{CH}(\text{COOH})\text{NH}_2$ .
- Iodogluten.**—Preparation of vegetable albumin containing 8% I.
- Iedolen.**—Combination of iodol (tetra-iodopyrrole) and albumin; contains 30% idol.
- Iodolin.**—Quinoline chloromethyliodochloride,  $\text{C}_9\text{H}_7\text{N}(\text{CH}_2\text{Cl})\text{ClI}$ .
- Iodolinum.** See iodolin.
- Iodolysin.**—Preparation similar to iodine; contains 43% thiosinamine and 47% I.
- Iodomenim.**—Iodised casein containing bismuth (10% I).
- Iodophenin.**—Tri-iodophenacetin.
- Iodoprotein.**—Albumin preparation containing 10% I.
- Iodozol.**—Di-iodo-*p*-phenolsulphonic acid,  $\text{C}_6\text{H}_2\text{I}_2(\text{OH})\text{SO}_3\text{H}.3\text{H}_2\text{O}$ .
- Iodylin.**—Bismuth iodosalicylate.
- Iodylolorm.**—Iodised gelatin (10% I).
- Iohydrin.**—Di-iodoisopropyl alcohol,  $\text{CH}_2\text{I}.\text{CH}(\text{OH}).\text{CH}_2\text{I}$ .
- Iothion.** See iohydrin.
- Isarol.**—See ichthosulphol.
- Isoform.**—*p*-Iodoxyanisole,  $\text{CH}_3\text{O}.\text{C}_6\text{H}_4.\text{IO}_2$ .
- Isopral.**—Trichloroisopropyl alcohol,  $\text{CCl}_3.\text{CH}(\text{OH}).\text{CH}_3$ .
- Istizin.**—1.8-Dihydroxyanthraquinone.
- Jacovol.**—Emulsion of cod-liver oil with glycerophosphates of sodium, calcium, and iron.
- Joha.**—Solution of 40% of salvarsan in iodinol.
- Kachin.**—A pyrocatechol photographic developer.
- Kakodyljacol.** See cacodyliacol.
- Kalmopyrin.**—Calcium acetylsalicylate,  $(\text{C}_2\text{H}_3\text{O}.\text{OC}_6\text{H}_4.\text{COO})_2\text{Ca}$ .
- Kalzose.**—Casein preparation containing calcium.
- Kephaldol.**—Preparation made from phenetidine and salicylic and citric acids.
- Kinetine.**—Combination of quinine and hectine.
- Kineurine.**—Quinine glycerophosphate,  $\text{C}_9\text{H}_7\text{O}_3\text{H}_2\text{PO}_3(\text{C}_{20}\text{H}_{23}\text{N}_2\text{O}_2)_2.4\text{H}_2\text{O}$ .
- Koronium bromide.**—Strontium bromide,  $\text{SrBr}_2.6\text{H}_2\text{O}$ .
- Krelos.**—Mixture of tar distillates and rosin soap solution.
- Kresogol.** See kresogol.
- Kresosteril.** See kresosteril.
- Kryogenin.** See kryogenin.
- Kynurin.**—*p*-Hydroxyquinoline,  $\text{C}_9\text{H}_6(\text{OH})\text{N}$ .
- Lactagol.**—Powdered extract of cotton-seed.
- Lactanin.**—Bismuth bilacto-monotannate.
- Lacteol.**—Preparation of lactic acid bacilli.
- Lactigen.** See lacteol.
- Lactiloids.** See lacteol.
- Lactobaccilline.** See lacteol.
- Lactone.** See lacteol.
- Laxans.** See purgen.
- Laxatol.** See purgen.
- Laxen.** See purgen.
- Laxoin.** See purgen.
- Lecithol.**—Lecithin from egg yolk.
- Lecutyl.**—Combination of lecithin and copper cinnamate (1.5% Cu).
- Lenicet.**—Basic aluminium acetate,  $\text{Al}_2(\text{OH})_2(\text{C}_2\text{H}_3\text{O}_2)_4.\text{H}_2\text{O}$ .
- Lentin.**—*m*-Phenylenediamine hydrochloride,  $\text{C}_6\text{H}_4(\text{NH}_2)_2.2\text{HCl}$ .
- Leptynol.**—Colloidal palladous hydroxide suspended in sesamé oil.
- Leucoline.**—Quinoline,  $\text{C}_9\text{H}_7\text{N} \begin{matrix} \text{CH} : \text{CH} \\ \text{N} : \text{CH} \end{matrix}$ .
- Levurargyre.**—Mercury compound of nucleoprotein.
- Levuretin.**—Dried yeast cells.
- Levurinoze.** See levuretin.
- Lipobromol.**—Brominated poppyseed oil (33% Br).
- Lipoiodin.**—Di-iodobrassic acid ethyl ester,  $\text{C}_{19}\text{H}_{39}\text{Cl} : \text{Cl}.\text{CO}_2\text{C}_2\text{H}_5$ .
- Lithium-diuretin.**—Addition product of theobrominelithium and lithiumsalicylate,  $\text{C}_7\text{H}_7\text{N}_4\text{O}_2\text{Li}.\text{HO}.\text{C}_6\text{H}_4.\text{CO}_2\text{Li}$ .
- Lithyol.** See ichthosulphol.
- Lodal.**—An oxidation product of laudanoline.
- Lofotol.**—Cod-liver oil charged with carbon dioxide.
- Lucidol.**—Benzoyl peroxide  $(\text{C}_6\text{H}_5.\text{COO})_2\text{O}_2$ .
- Luesan.**—Glidine preparation containing mercury.
- Luminal.**—Phenyl ethyl malonylurea,  $\begin{matrix} \text{C}_2\text{H}_5 \\ \text{C}_6\text{H}_5 \end{matrix} \text{C} \begin{matrix} \text{CO}.\text{NH} \\ \text{CO}.\text{NH} \end{matrix} \text{CO}$ .
- Lycin.** See acidol.
- Lygosin.**—Di-hydroxydibenzalacetone,  $\text{HO}.\text{C}_6\text{H}_4.\text{CH} : \text{CH}.\text{CO}$ .
- Lysochlor.** Chloro-*m*-cresol,  $\text{C}_6\text{H}_3\text{Cl}(\text{CH}_3)\text{OH}$ .
- Lysoform.**—A liquid formaldehyde potassium soap.
- Magnesium-perhydrol.**—Mixture containing magnesia and 15 or 25%  $\text{MgO}_2$ .
- Malonal.** See veronal.
- Malourea.** See veronal.
- Maltyl.**—Dry malt extract; contains about 90% of soluble carbohydrates.
- Maretin.**—*m*-Tolylsemicarbazide,  $\text{CH}_3.\text{C}_6\text{H}_4.\text{NH}.\text{NH}.\text{CO}.\text{NH}_2$ .
- Maricol.**—Magnesium ricinoleate,  $(\text{HO}.\text{C}_{17}\text{H}_{32}\text{CO}_2)_2\text{Mg}$ .
- Medinal.**—Sodium compound of veronal.
- Melrubin.**—Sodium 1-phenyl-2.3-dimethylpyrazolone-4-aminomethane sulphonate,  $\text{C}_{11}\text{H}_{11}\text{N}_2\text{O}.\text{NH}.\text{CH}_2.\text{SO}_3\text{Na}$ .
- Melubrin.**—Mercury salicylsulphonate.
- Menthophenol.**—Mixture of phenol 1, menthol 3 parts.
- Mercuriocolo.**—Double oleate of cholesterol and mercury.
- Mergal.**—A combination of mercury cholate and albumin tannate.
- Merjodin.**—Mercury di-iodophenol-*p*-sulphonate,  $(\text{HO}.\text{C}_6\text{H}_2\text{I}_2.\text{SO}_3)_2\text{Hg}$ .
- Merlusan.**—Mercury compound of tyrosine (53% Hg),  $\text{C}_9\text{H}_9\text{O}_2\text{NHg}$ .
- Merochinal.**—Mercury hydroxyquinolinesulphonate,  $(\text{HO}.\text{C}_6\text{H}_3\text{N}.\text{SO}_3)_2\text{Hg}$ .



**Mesotan.**—Salicylic methoxymethyl ester,  
 $\text{HO.C}_6\text{H}_4.\text{COO.CH}_2.\text{OCH}_3$ .  
**Methozin.**—Antipyrine (phenyldimethylpyrazo-  
 lone,



**Methylrhodin.**—Methyl acetylsalicylate,  
 $\text{C}_2\text{H}_5\text{O.O.C}_6\text{H}_4.\text{CO}_2\text{CH}_3$ .

**Metoquinone.**—Addition product of metol  
 (methyl-*p*-aminophenol) and quinol,  
 $\text{C}_6\text{H}_4[\text{HO(CH}_3\text{)NH.C}_6\text{H}_4.\text{OH}]_2$ .

**Metramine.** See hexamine.

**Migralgine.**—Mixture of antipyrine 88, caffeine  
 9, and salicylic acid 3 parts, fused together.

**Momordicine.**—Elaterin,  $\text{C}_{20}\text{H}_{28}\text{O}_5$ .

**Monotal.**—Guaiacol methyl glycollate,  
 $\text{CH}_2(\text{OCH}_3).\text{COOC}_6\text{H}_4.\text{OCH}_3$ .

**Morphosan.**—Morphine methyl bromide,  
 $\text{C}_{17}\text{H}_{19}\text{O}_3\text{N.CH}_3\text{Br.H}_2\text{O}$ .

**Mucogeene.**—An anthraquinone derivative,  
 $\text{C}_{13}\text{H}_{15}\text{N}_2\text{O}_2\text{Cl}$ .

**Mydrasine.**—Atropine methyl bromide,  
 $\text{C}_{17}\text{H}_{23}\text{NO}_3.\text{CH}_3\text{Br}$ .

**Naphtholsalol.**— $\beta$ -Naphthyl salicylate,  
 $\text{HO.C}_6\text{H}_4.\text{COO.C}_{10}\text{H}_7$ .

**Nareryl.**—Ethylmarceine hydrochloride,  
 $\text{C}_{23}\text{H}_{26}(\text{C}_2\text{H}_5)\text{NO}_8.\text{HCl}$ .

**Nargol.**—Silver nucleinate (10 % Ag).

**Nealpon.** See pantopon.

**Neoform.**—Bismuth compound of tri-iodophenol,  
 $\text{C}_6\text{H}_2\text{I}_3\text{OBi(OH)}_2.\text{Bi}_2\text{O}_3$ .

**Neoleptol.**—Triformyltrimethylenetriamine.

**Neopine.**—Hydroxycodine,  $\text{C}_{18}\text{H}_{20}\text{NO}_3(\text{OH})$ .

**Neopyrin.**—Valerylaminopyrazine.

**Neosalvarsan.**—Sodium 3,3'-diamino-4,4'-dihy-  
 droxy-arsenobenzene-formaldehyde sulphony-  
 late,

$\text{NH}_2.\text{C}_6\text{H}_3(\text{OH})\text{As.As.C}_6\text{H}_3(\text{OH})\text{NH(CH}_2\text{O)SONa}$ .

**Neosode.**—Iodocatechin ( $\text{O}_{15}\text{H}_{14}\text{O}_6.3\text{H}_2\text{O}$ )<sub>3</sub>I.

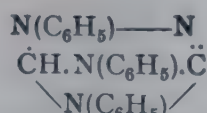
**Nerolin.**— $\beta$ -Naphthyl methyl ether,  $\text{C}_{10}\text{H}_7\text{O.CH}_3$ .

**Neuraltein.**—Sodium *p*-ethoxyphenylaminome-  
 thane sulphonate,



**Neuronal.**—Diethylbromo-acetamide,  
 $(\text{C}_2\text{H}_5)_2\text{CBr.CO.NH}_2$ .

**Nitron.**—1,4-Diphenyl-3,5-endanilodihydrotriaz-  
 zole,



**Nizin.**—Zinc sulphanilate,  $(\text{NH}_2.\text{C}_6\text{H}_4.\text{SO}_3)_2\text{Zn}$ .

**Novargan.**—Protein preparation containing 10 %  
 Ag.

**Novaspirin.**—Methylenecitrylsalicylic acid.

**Novatophan.**—Ethyl 6-methyl-2-phenylquinoline-  
 4-carboxylate,  $\text{C}_8\text{H}_5.\text{C}_9\text{H}_4\text{N(CH}_3\text{)COOC}_2\text{H}_5$ .

**Noviform.**—Bismuth compound of tetrabromo-  
 pyrocatechol.

**Novocaine.**—*p*-Aminobenzoylethylaminoethanol  
 hydrochloride,



**Novocol.**—Sodium monoguaiacol phosphate.

**Nucleogen.**—Preparation containing iron nuc-  
 leinate and arsenic.

**Oleanodyne.**—Preparation containing oleic acid,  
 aconitine, atrophine, morphine, and veratrine.

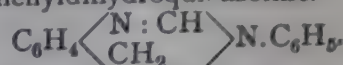
**Oleogualacol.**—Guaiacol oleate,  
 $\text{CH}_3\text{O.C}_6\text{H}_4\text{O.CO.C}_{17}\text{H}_{35}$ .

**Omnopon.** See pantopon.

**Omorol.** See novargan.

**Optochin.**—Ethylhydrocupreine.

**Orexin.**—Phenyldihydroquinazoline.



**Orsudan.**—Sodium methyl acetyl-*p*-aminophenyl  
 arsiniate,



**Ortizon.** See hyperol.

**Ovoferrin.**—Vitellin preparation containing iron.

**Oxylith.**—Sodium peroxide.

**Oxyntin.**—A combination of albumin and hydro-  
 chloric acid.

**Palmiacol.** See cetiacol.

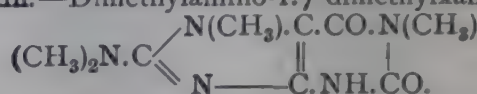
**Pantopon.**—Mixture of the soluble hydrochlorides  
 of opium alkaloids.

**Parabismut.**—Bismuth paranucleinate.

**Paracodine.**—Dihydrocodeine,  
 $\text{C}_{17}\text{H}_{19}(\text{OCH}_3)(\text{OH})\text{NO}$ .

**Paralysol.**—Solid cresol preparation,  
 $\text{C}_6\text{H}_4(\text{CH}_3)\text{OK}, 3\text{C}_6\text{H}_4(\text{CH}_3)\text{OH}$ .

**Paraxin.**—Dimethylamino-1,7-dimethylxanthine.



**Pegnine.**—Preparation of lactose and rennet.

**Pellidol.**—Diacetylaminazotoluene.

**Pepsalia.**—Preparation of pepsin and sodium  
 chloride.

**Perborax.**—Sodium perborate,  $\text{NaBO}_3.4\text{H}_2\text{O}$ .

**Perborol.** See perborax.

**Perhydrit.** See hyperol.

**Perhydrol.**—Solution of hydrogen peroxide, 100  
 vol., or 30 % by weight.

**Permidan.**—Dimethylaminopyrazolone,  
 $\text{C}_8\text{H}_9\text{N}_3\text{O}$ .

**Phenalglin.**—Phosphoammonioacetanilide.

**Phenamine.**—Amino-acet-*p*-phenetidine hydro-  
 chloride,



**Phenolax.** See purgen.

**Phenosol.**—Monophenetidine of salicylacetic acid,  
 $\text{COOH.C}_6\text{H}_4.\text{O.CH}_2.\text{CO.NH.C}_6\text{H}_4.\text{OC}_2\text{H}_5$ .

**Phenoval.**—Bromovalerylphenetidine,  
 $\text{C}_4\text{H}_8\text{Br.CO.NH.C}_6\text{H}_4.\text{OC}_2\text{H}_5$ .

**Phenyform.**—Condensation product of phenol  
 and formaldehyde.

**Phenylon.** See methozin.

**Phobrol.**—50 % solution of chloro-*m*-cresol in  
 potash castor oil soap.

**Photoxylin.** See celloidin.

**Picrastol.**—Dimethyloldiformylmethenyltetrame-  
 thylenepentamine,  $\text{C}_9\text{H}_{17}\text{N}_5\text{O}_4$ .

**Picratol.**—Silver picrate.

**Pinakol.**—A pyrogallol photographic developer in  
 which part of the alkali usually employed is  
 replaced by sodium aminoacetate.

**Piral.**—Pyrogallol,  $\text{C}_6\text{H}_3(\text{OH})_3$ .

**Plecavol.**—Consists chiefly of *p*-aminobenzoyleu-  
 genol,  $\text{NH}_2.\text{C}_6\text{H}_4.\text{CO.O.C}_6\text{H}_3(\text{C}_2\text{H}_5)\text{OCH}_3$ ,  
 tricresol (a mixture of the three cresols), and  
 formaldehyde.

**Pleistopon.**—Similar to pantopon, except that it  
 contains no narcotine.

**Pneumin.**—Condensation product of creosote and  
 formaldehyde.

**Pneumosan.**—Amyl thiotrimethylamine.

**Propæsin.**—Propyl ester of *p*-aminobenzoic acid,  
 $\text{NH}_2.\text{C}_6\text{H}_4.\text{COOC}_3\text{H}_7$ .



**Proponal.**—Dipropylbarbituric acid,



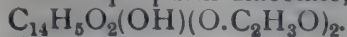
**Proposote.**—Creosote phenylpropionate.

**Protosal.**—Salicyclic acid glycerol formal ester,



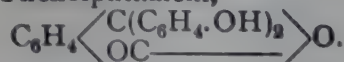
**Protylin.**—Albumin preparation containing phosphorus.

**Purgatin.**—Anthrapurpurin diacetate,



**Purgatol.** See purgatin.

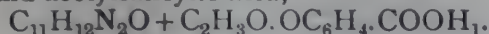
**Purgen.**—Phenolphthalein,



**Pyoktanin.**—Methyl violet,



**Pyracetosalyl.**—Addition product of antipyrine and acetylsalicylic acid,



**Pyrobromone.**—Bromodimethylaminoantipyrine.

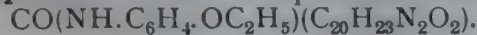
**Pyronal.**—Antipyrine salicylacetate,



**Pyrophan.**—Combination of pyrogallol and dimethylamine.

**Quietol.**—Dimethylaminodimethylisovalerylpropyl ester hydrobromide.

**Quinaphenin.**—Phenetidine quinine carbonic ester,



**Quinaphthol.**—Quinine  $\beta$ -naphtholsulphonate,



**Quineonal.**—Compound of quinine and veronal.

**Quinine lygosinate.**—Dihydroxydibenzalacetone-quinine,



**Quinoform.**—Quinine formate,  $C_{20}H_{24}N_2O_2$ ,  $HCOOH$ ; also a condensation product of cinchotannic acid and formaldehyde.

**Quinopyrin.**—A combination of antipyrine, 2, and quinine hydrochloride, 3 parts.

**Quinosol.**—Mixture of hydroxyquinoline and potassium sulphates,  $C_9H_6NOSO_3K, 4H_2O$ .

**Quinotropin.**—Hexamethylenetetramine quinate,  $C_6H_{12}N_4, C_6H_7(OH)_4CO_2H$ .

**Regulin.**—Broken-up agar-agar with 25 % of Cascara-extract

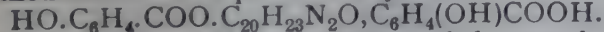
**Resaldol.**—Resorcybenzoic acid ethyl ester,



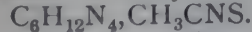
**Rexotan.**—Methylenhtannin-urea,



**Rheumatin.**—Saloquinine salicylate,



**Rhodaform.**—Addition product of hexamethylenetetramine and methyl thiocyanate,



**Riopan.**—Soluble brown powder containing 50 % of ipecacuanha alkaloids in the form of their hydrochlorides.

**Rongalite C.** See hydrosulphite N.F. extra.

**Sabromine.**—Calcium dibromobehenate (29 % Br),  $(C_{22}H_{41}O_2Br_2)_2Ca$ .

**Sajodin.**—Calcium moniodobehenate,  $(C_{22}H_{42}O_2I)_2Ca$ .

**Salacetin.** See acetosal.

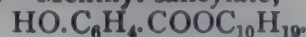
**Saletin.** See acetosal.

**Salibromin.**—Dibromosalicylic methyl ester,



**Salicreol.**—Creosote salicylate.

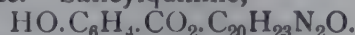
**Salimenthol.**—Menthyl salicylate,



**Salit.**—Bornyl salicylate,  $HO.C_6H_4.COO.C_{10}H_{17}$ .

**Salocreol.** See salicreol.

**Saloquinine.**—Salicylquinine,



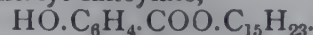
**Salufer.**—Sodium silicofluoride.

**Salvarsan.**—Dihydroxydiaminoarsenobenzene dihydrochloride,  $HCl.NH_2(OH)C_6H_3.As.As$ ,  $C_6H_3(OH)NH_2.HCl, 2H_2O$ .

**Salvarsan, New.** See neosalvarsan.

**Santheose.**—Theobromine,  $C_5H_2(CH_3)_2N_4O_2$ .

**Santyl.**—Santalyl salicylate,



**Sauerin.**—Preparation of lactic acid bacilli.

**Savore.**—Preparation of milk, cereal proteins and albumoses, and carbohydrates.

**Scopomorphine.**—Sterilised solution containing per c.c., 0.0006 gm. of euscopol and 0.015 gm. of morphine hydrochloride.

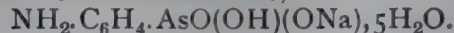
**Sedeff.**—Effervescent preparation containing opium, bismuth, and digestive ferments.

**Sennatin.**—Preparation containing the active principles of senna leaves.

**Sennax.**—Preparation containing the water-soluble glucosides of senna leaves.

**Sidonal, New.**—Mixture of quinic acid,  $C_6H_7(OH)_4CO_2H$ , and its anhydride.

**Soamin.**—Sodium arsanilate,



**Solulol.**—Thymic acid (nucleotinphosphoric acid),  $C_{30}H_{46}N_4O_{15}(P_2O_5)_2$ .

**Somnoform.**—Mixture of ethyl chloride 60, methyl chloride 35, and ethyl bromide 5 %.

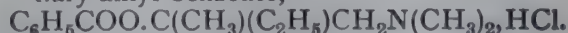
**Sophol.**—Silver formonucleinate (20 % Ag).

**Spirarsyl.**—Sodium salt of arsenophenylglycine,  $(CO_2Na.CH_2.NH.C_6H_4)_2As_2$ .

**Spirosal.**—Monoglycol ester of salicylic acid,  $HO.C_6H_4.COO.CH_2.CH_2OH$ .

**Stearosan.**—Compound of santalol and stearic acid.

**Stovaine.**—Hydrochloride of dimethylamino tertiary amyl benzoate,



**Styptol.**—Cotarnine phthalate,



**Subcutin.**—Anæsthesin phenolsulphonate,



**Sublamine.**—Mercuric ethylenediamine sulphate (43 % Hg).

**Sucramine.**—Ammonium salt of saccharin.

**Sulfoid.**—Preparation of colloidal sulphur (80 % S) with an albuminous substance as protective colloid.

**Sulphoform.**—Triphenylstibine sulphide,  $(C_6H_5)_3SbS$ .

**Suprarenaline.** See epinephrine.

**Suprarenine.** See adrenaline.

**Synthalin.**—Piperonylquinolinecarboxylic acid methyl ester,  $CH_2O_2.C_6H_3.C_9H_5N.COOCH_3$ .

**Syrgol.**—Colloidal silver.

**Tachiol.**—Silver fluoride.

**Tanargan.**—A combination of tannin and silver albuminate.

**Tanninphenolmethane.**—Condensation product of tannin, formaldehyde, and phenol.

**Tanninthymolmethane.**—Condensation product of tannin, formaldehyde, and thymol.

**Tannismuth.**—Bismuth bitannate.

**Tannisol.**—Methyleneditannin  $(C_{14}H_9O_6)_2CH_2$ .



- Tannobromine.**—A combination of dibromotannin and formaldehyde.
- Tannocreosoform.**—Condensation product of tannin, formaldehyde, and creosote.
- Tannoguaiaform.**—Condensation product of tannin, formaldehyde, and guaiacol.
- Tannothymal.** See tanninthymolmethane.
- Tannyl.**—Oxychlorocasein tannate.
- Tenosin.**—Solution containing, per c.c., 0.0005 gm. of  $\beta$ -iminazolyethylamine and 0.02 gm. of *p*-hydroxyphenylethylamine.
- Testijodyl.**—Combination of coagulated blood albumin and iodine.
- Theobromose.**—Lithium compound of theobromine,  $C_7H_7N_4O_2Li$ .
- Theocin.**—Sodium compound of theobromine,  $C_7H_7N_4O_2Na$ .
- Theolactin.**—Addition product of theobromine-sodium and sodium lactate.
- Theosalin.**—Addition product of theobromine-sodium and sodium sulphosalicylate,  $C_7H_7N_3O_2Na, C_7H_5O_3, SO_3Na$ .
- Thephorin.**—Addition product of theobromine-sodium and sodium formate,  $C_7H_7N_4O_2Na, HCO_2Na, H_2O$ .
- Thermiol.**—Sodium phenylpropionate,  $C_6H_5.C : C.CO_2Na$ .
- Thiallon.**—Preparation containing sodium sulphate (26 %), citrates of sodium (56), potassium (3) and lithium (3), sodium chloride (3), and water (9 %).
- Thigenol.**—Sodium salt of ichthoform (condensation product of ichthyol and formaldehyde).
- Thiophysem.** See tiidine.
- Tholaform.**—Mixture of equal parts of menthol and trioxymethylene.
- Throphleol.**—56 % solution of erythrophleine hydrochloride (from casca bark) in eugenol.
- Thymatol.**—Thymol carbonate,  $CO(O.C_{10}H_{13})_2$ .
- Thymegol.**—Mercury potassium salt of thymol-*p*-sulphonate.
- Thymolin.**—Mixture of naphthalene 18, camphor 1, and thymol 1 part.
- Thymoloform.**—Condensation product of formaldehyde and thymol.
- Thyresol.**—Santalol methyl ether,  $C_{15}H_{23}O.CH_3$ .
- Tiodine.**—Thiosinamine ethyl iodide,  $C_3H_5.NH.CS.NH_2, C_2H_5I$ .
- Toxynon.**—Sodium *m*-acetylaminomercuribenzoate,  $HgOH.C_6H_3(NH.C_2H_5O)CO_2Na$ .
- Tricalcol.**—Colloidal combination of tricalcium phosphate and albumin.
- Tricarbin.** See glycarbin.
- Triferrin.** See ferrinol.
- Trigemin.**—Compound of butyl chloral hydrate and pyramidone (dimethylaminoantipyrine).
- Trilactine.**—Preparation of lactic acid bacilli.
- Trinitrin.**—Nitroglycerin.
- Trixidol.**—An emulsion of antimony trioxide (30 %  $Sb_2O_3$ ).
- Tryen.** See griserin, novum.
- Trygase.**—Dried yeast cells.
- Trypan Red.**—Prepared from tetrazotised benzenesulphonic acid and 2 mols. of sodium naphthylaminedisulphonate,  $(SO_3H)C_6H_3.N_2.C_{10}H_4(SO_3Na)_2NH_2, C_6H_4.N_2.C_{10}H_4(SO_3Na)_2NH_2$ .
- Tryparosan.**—Chlorinated parafochsin.
- Tylcalsin.** See kalmopyrin.
- Tyllithin.** See apyron.
- Tylmarin.**—Acetyl-*o*-coumaric acid,  $C_2H_3O.OC_6H_4.CH : CH.CO_2H$ .
- Tylnatrin.**—Sodium acetylsalicylate,  $C_2H_3O.OC_6H_4.COONa$ .
- Tyramine.**—*p*-Hydroxyphenylethylamine hydrochloride,  $HO.C_6H_4.C_2H_4.NH_2, HCl$ .
- Ulmarene.** See mesotan.
- Unal.**—Alkali salt of *p*-aminophenol hydrochloride; *rodinal* is the concentrated solution.
- Uraminoantipyrin.**—Antipyrilurea,  $NH_2.CO.NH.C_{11}H_{11}N_2O$ .
- Urapurgol.** See helmitol.
- Urea-bromine.**—Combination of urea and calcium bromide (36 % Br),  $4CO(NH_2)_2, CaBr_2$ .
- Uritone.** See hexamine.
- Urocitral.**—Addition product of theobromine-sodium and sodium citrate.
- Urodonal.**—Granular preparation of hexamethylenetetramine, sidonal (piperazine quinate), and lysidine (methylglyoxalidine).
- Urogenin.**—Addition product of theobromine and lithium hippurate,  $C_7H_8N_4O_2, C_6H_5.CO.NH.CH_2.CO_2Li$ .
- Urol.**—Urea quinate.
- Urosin.**—Lithium quinate,  $C_6H_7(OH)_4COOLi$ .
- Urotropine, New.** See helmitol.
- Valamin.**—Isovaleric ester of tertiary amyl alcohol.
- Valearin.**—Valeryltrimethylammonium chloride.
- Valisan.**—Bornylbromoisovalerate,  $C_4H_8BrCO.OC_{10}H_{17}$ .
- Valyl.**—Valeric diethylamide,  $C_4H_9.CO.N(C_2H_5)_2$ .
- Veronal.**—Diethylbarbituric acid (diethylmalonylurea),  $(C_2H_5)_2C \begin{matrix} \diagup CO.NH \\ \diagdown CO.NH \end{matrix} CO$ .
- Veropyrin.**—Mixture of dionine (ethylmorphine hydrochloride) 0.01, veronal-sodium 0.2, and kalmopyrin, 0.5 part.
- Vesalvine.** See hexamine.
- Vesipyrine.**—Phenyl acetylsalicylate,  $CH_3.CO.OC_6H_4.COOC_6H_5$ .
- Vimopyrin.**—*p*-Phenetidine tartrate.
- Vioform.**—Hydroxyquinoline chloriodide,  $C_9H_6N(OH)ICl$ .
- Vitafer.**—Preparation of milk and glycerophosphates of calcium and sodium.
- Xaxa.** See acetosal.
- Xaxaquin.**—Quinine acetylsalicylate,  $C_{20}H_{24}N_2O_2, CH_3CO.OC_6H_4.COOH$ .
- Yara-yara.** See nerolin.
- Yatren.** See griserin, novum.
- Zymin.**—Special dry powdered yeast.



## NEWER PROPRIETARY AND TRADE NAMES.

- Acetylarsan** (Diethylamine acetyl-amino-oxy-phenylarsonate) May & Baker, Ltd.
- Adaprin** (Tablets of nicotinamide and vitamin K) Ward, Blenkinsop & Co., Ltd.
- Adexolin** (Preparations containing vitamins A and D concentrate) Glaxo Laboratories, Ltd.
- Adinol** (Vitamin A and D capsules) Duncan Flockhart & Co., Ltd.
- Adrenatone** (Adrenalin injections) Duncan Flockhart & Co., Ltd.
- Adrenutol** (Adrenalin injection) Evans Medical Supplies, Ltd.
- Advita** (Vitamins A and D preparations) Lever Bros. and Unilever, Ltd.
- Agotan** (Phenylcinchoninic acid; powders, tablets, ointment) Howards & Sons, Ltd.
- Allodene** (Amphetamine) W. J. Bush & Co., Ltd.
- Allonal** (Allyl-isopropyl-barbiturate of amidopyrine) Roche Products, Ltd.
- Alopon** (Hydrochlorides of opium alkaloids) Allen & Hanburys, Ltd.
- Amabevan** (Carbarsone tablets) Evans Medical Supplies, Ltd.
- Amandol** (Benzaldehyde) May & Baker, Ltd.
- Ambamide** (*p*-amino methyl-benzene-sulphonamide) R. F. Reed, Ltd.
- Ambinon** (Anterior pituitary gonadotrophic-thyrotrophic fractions) Organon Laboratories, Ltd.
- Amfix** (Ultra-rapid photographic fixer) May & Baker, Ltd.
- Ammoket** (Ammonium mandelate elixir) Boots Pure Drug Co., Ltd.
- Anacardone** (Nikethamide B.P.) The British Drug Houses, Ltd.
- Anahaemin** (Pharmaceutical liver preparations) The British Drug Houses, Ltd.
- Anahepol** (Concentrated liver anti-anaemic principle) Allen & Hanburys, Ltd.
- Analjol** (Analgesic and counter-stimulant liniment) Kaylene, Ltd.
- Andelix** (Ammonium mandelate elixir) The British Drug Houses, Ltd.
- Anethaine** (Amethocaine hydrochloride) Glaxo Laboratories, Ltd.
- Aneurex** (Preparations of vitamin B<sub>1</sub>) Evans Medical Supplies, Ltd.
- Anthiomaline** (Lithium antimony thiomalate) May & Baker, Ltd.
- Anthisan** (Anti-histaminic agents, N-dimethyl-aminoethyl, N-p-methoxybenzyl  $\alpha$ -aminopyridine maleate) May & Baker, Ltd.
- Antrypol** (Suramin B.P.) Imperial Chemical (Pharmaceuticals), Ltd.
- Apercara** (Aromatic cascara sagrada) Duncan Flockhart & Co., Ltd.
- Arcanol** (Methyl phenylcinchoninate and acetylsalicylic acid compound) British Schering, Ltd.
- Arecan** (Injection of procain adrenalin, etc.) Evans Medical Supplies, Ltd.
- Arthrytin** (Calcium ortho-iodoxybenzoate) May & Baker, Ltd.
- Arvitin** (Silver vitellin) Johnsons of Hendon, Ltd.
- Ascabiol** (Benzyl benzoate emulsion) May & Baker, Ltd.
- Asensitine** (Dental local anaesthetic) Duncan Flockhart & Co., Ltd.
- Asmodrin** (Asthma inhalent) Duncan Flockhart & Co., Ltd.
- Aspirgran** (Acetylsalicylic acid B.P.C., granular crystals) Monsanto Chemicals, Ltd.
- Astevan** (Inhalation solution for asthma) Evans Medical Supplies, Ltd.
- Astryl** (Sodium p-glycolyl arsanilate) May & Baker, Ltd.
- Atophan** (Phenylcinchoninic acid preparations) British Schering, Ltd.
- Atophanyl** (Sodium phenylcinchoninate and sodium salicylate solution) British Schering, Ltd.
- Auro-Calcium** (Non-toxic gold preparations) The Crookes Laboratories, Ltd.
- Avloprocil** (Procaine penicillin oily injections) Imperial Chemical (Pharmaceuticals), Ltd.
- Avoleum** (Highly concentrated solution of vitamin A) The British Drug Houses, Ltd.
- Azol** (Paramidophenol hydrochloride in solution) Johnsons of Hendon, Ltd.
- Beflavit** (Vitamin B<sub>2</sub> (riboflavin) preparations) Roche Products, Ltd.
- Benadon** (Pyridoxine, vitamin B<sub>6</sub> preparations) Roche Products, Ltd.
- Benerva** (Vitamin B<sub>1</sub>, preparations) Roche Products, Ltd.
- Benerva Compound** (Vitamin B<sub>1</sub>, B<sub>2</sub> and nicotinamide) Roche Products, Ltd.
- Benzevan and Benzevan Cream** (Sarcopticide containing benzyl benzoate) Evans Medical Supplies, Ltd.
- Berin** (Vitamin B<sub>1</sub>) Glaxo Laboratories, Ltd.
- Biarsamide** (Bismuth tryarsamide) May & Baker, Ltd.
- Bilectol** (Pheniodol preparations) The British Drug Houses, Ltd.
- Biliselectan** ( $\beta$ -(4-hydroxy-3, 5-diiodophenyl)- $\alpha$ -phenyl-propionic acid (pheniodol) preparations) British Schering, Ltd.



- Bisalevan** (Bismuth salicylate injection) Evans Medical Supplies, Ltd.
- Bisantol** (Bismuth salicylate in oil) May & Baker, Ltd.
- Bisglucol** (Bismuth metal in isotonic solution) May & Baker, Ltd.
- Bismecol** (Bismuth ethyl camphorate solution) May & Baker, Ltd.
- Bismevan** (Injection of bismuth metal) Evans Medical Supplies, Ltd.
- Bismostab** (Bismuth metal in isotonic solution) Boots Pure Drug Co., Ltd.
- Borocaine** (Procaine borate) The British Drug Houses, Ltd.
- Butesin Picrate** (Analgesic and antiseptic ointment) Abbott Laboratories (England), Ltd.
- Butyn** (Local anaesthetic) Abbott Laboratories (England), Ltd.
- Caffedrin** (Elixir caffeine iodide with ephedrine) Duncan Flockhart & Co., Ltd.
- Caffodine** (Caffeine iodide) Duncan Flockhart & Co., Ltd.
- Calcidrine Syrup** (Calcium iodide and pentobarbitone) Abbott Laboratories (England), Ltd.
- Calcium-D-Redoxon** (Vitamins C and D with calcium) Roche Products, Ltd.
- Calcium Kemball** (Calcium gluconate) Kemball, Bishop & Co., Ltd.
- Caldimil** (Calcium sodium lactate with vitamin D) The British Drug Houses, Ltd.
- Calobor G.** (Calcium borogluconate) Genatosan, Ltd.
- Calsimil** (Calcium sodium lactate with vitamin D) The British Drug Houses, Ltd.
- Calsolact** (Calcium sodium lactate) Allen & Hanburys, Ltd.
- Calsprate** (Calcium acetylsalicylate) Genatosan, Ltd.
- Caprisin** (Capryl hydrocupreinotoxin hydrochloride) Howards & Sons, Ltd.
- Cardophyllin** (Theophylline with ethylenediamine) Whiffen & Sons, Ltd.
- Celin** (Vitamin C) Glaxo Laboratories, Ltd.
- Cestarsol** (Arecoline acetarsol) May & Baker, Ltd.
- Chilvit** (Nicotinic acid) R. F. Reed, Ltd.
- Chloryl Anaesthetic** (Pure ethyl chloride) Duncan Flockhart & Co., Ltd.
- Chlorylen** (Trichlorethylene inhalant) British Schering, Ltd.
- Cholectrin** (Dehydrocholic acid and sodium dehydrocholate preparations) The British Drug Houses, Ltd.
- Cholectrina** (Dehydrocholic acid and sodium dehydrocholate preparations) The British Drug Houses, Ltd.
- Cholectropine** (Dehydrocholic acid and sodium dehydrocholate preparations) The British Drug Houses, Ltd.
- Cincaine** (Isopropyl hydrocupreine (cincaine) hydrochloride) Howards & Sons, Ltd.
- Clinestrol** (Stilboestrol) Glaxo Laboratories, Ltd.
- Colistatin** (Succinyl sulphathiazole) Herts Pharmaceuticals, Ltd.
- Cortiron** (Desoxycorticosterone acetate preparations) British Schering, Ltd.
- Cortrophin** (Anterior pituitary adrenocorticotrophic hormone) Organon Laboratories, Ltd.
- Corvotone** (Nikethamide) Boots Pure Drug Co., Ltd.
- Cyclonal** (Hexobarbitone) May & Baker, Ltd.
- Cyclonal Sodium** (Soluble hexobarbitone) May & Baker, Ltd.
- Cylotropin** (Hexamine, sodium salicylate, caffeine compound) British Schering, Ltd.
- Cystazol** (Hexamin sodium benzoate) Allen & Hanburys, Ltd.
- Cystopurin** (Hexamine sodium acetate) Genatosan, Ltd.
- Dastar** (Semi-refined cholesterol) Croda, Ltd.
- Davitamon** (Vitamin preparations) Organon Laboratories, Ltd.
- Dayamin** (Capsules containing vitamins A, B, C and D) Abbott Laboratories (England), Ltd.
- Dehydrocholin** (Dehydrocholic acid and sodium dehydrocholate preparations) The British Drug Houses, Ltd.
- Dekadexolin** (High potency vitamins A and D) Glaxo Laboratories, Ltd.
- Dermucid** (Sulphacetamide dermatological preparation) British Schering, Ltd.
- Diasone** (Disodium formaldehyde sulphonylate diamino diphenyl sulphone) Abbott Laboratories (England), Ltd.
- Diginutin** (Stable solution of digitalis leaf glycosides, physiologically standardized) Burroughs Wellcome & Co.
- Digitaline Granules** (Stable preparation of digitalis) Duncan Flockhart & Co.
- Dimenformon** (Oestradiol benzoate preparations) Organon Laboratories, Ltd.
- Doca** (Desoxycorticosterone acetate preparations) Organon Laboratories, Ltd.
- Dormigene** (Monobromisovalerylurea) Allen & Hanburys, Ltd.
- Durochrome** (Fast chrome mordant dyes) The Yorkshire Dyeware & Chemical Co., Ltd.
- Embazine** (Piperazine citrosalicylate preparation) May & Baker, Ltd.
- Embial** (Soluble barbitone) May & Baker, Ltd.
- Embryl** (Butobarbitone) May & Baker, Ltd.
- Emocin** (Acetylsalicylic acid lozenge) Burroughs Wellcome & Co.
- Empirin** (Acetylsalicylic acid) Burroughs Wellcome & Co.
- Ephregel** (Ephedrine and adrenalin nasal jelly) Evans Medical Supplies, Ltd.
- Ephresol** (Ephedrine and adrenalin nasal spray) Evans Medical Supplies, Ltd.
- Ephynal** (Synthetic vitamin E preparations) Roche Products, Ltd.
- Epicaïne** ("Epinine" and cocaine hydrochloride solution) Burroughs Wellcome & Co.
- Epinalin** (Adrenalin and ephedrine sulphate solution) Burroughs Wellcome & Co.
- Epinine** (3 : 4-Dihydroxyphenylethylmethanamine) Burroughs Wellcome & Co.



- Ergothane** (Ergotoxine ethanesulphonate solution) Evans Medical Supplies, Ltd.
- Essogen** (Preparation of vitamin A) Lever Bros. & Unilever, Ltd.
- Estersil** (Ethyl and propyl salicylglycollic esters) Johnsons of Hendon, Ltd.
- Estoform** (Orthoformic ester for medicinal use) The Crookes Laboratories, Ltd.
- Ethiodan** (Ethyl p-iodo-phenyl undecate) The British Drug Houses, Ltd.
- Eubion** (Vitamin A and D capsules) Evans Medical Supplies, Ltd.
- Eucupin** (Isoamyl hydrocupreine (Eucupin) bihydrochloride) Howards & Sons, Ltd.
- Evarsan** (Neoarsphenamine) Evans Medical Supplies, Ltd.
- Ferrofax** (Ferrous iron with vitamin D) The Crookes Laboratories, Ltd.
- Ferromalt** (Ferro-cuprum and vitamin D in malt extract) The Crookes Laboratories, Ltd.
- Ferro-Redoxon** (Vitamin C and ferrous iron) Roche Products, Ltd.
- Fersolate** (Preparation of ferrous sulphate exsic) Glaxo Laboratories, Ltd.
- Flavazole** (Sulphathiazole-proflavine) Boots Pure Drug Co., Ltd.
- Flavogel** (Acriflavine jelly) Glaxo Laboratories, Ltd.
- Fre-flo** (Acetylsalicylic acid) W. J. Bush & Co., Ltd.
- Gardenal** (Phenobarbital) May & Baker, Ltd.
- Gardenal Sodium** (Soluble phenobarbital) May & Baker, Ltd.
- Genaspirin** (Acetyl-salicylic acid tablets) Genatosan, Ltd.
- Genochrome** (Stabilised photographic colour developer) May & Baker, Ltd.
- Genophyllin** (Theophylline with ethylenediamine preparations) Genatosan, Ltd.
- Glucodin** (Glucose, vitamin D and calcium glycerophosphate) Glaxo Laboratories, Ltd.
- Glucophylline** (Theophylline and methyl glucamine) Abbott Laboratories (England), Ltd.
- Gonacrine** (Preparation of 2:8-diamino-10-methyl-acridinium chloride and diamino-acridine) May & Baker, Ltd.
- Gonan** (Chorionic gonadotrophin) The British Drug Houses, Ltd.
- Gonant** (Chorionic gonadotrophin) The British Drug Houses, Ltd.
- Gonazole** (Sulphathiazole with proflavine monohydrochloride) May & Baker, Ltd.
- Hexanastab** (Soluble hexabarbitone) Boots Pure Drug Co., Ltd.
- Iodicin** (Calcium iodoricinoleate) Burroughs Wellcome & Co.
- Iodolysin** (Thiosinaminethyl iodide) Allen & Hanburys, Ltd.
- Iradiostol** (Crystalline vitamin D<sub>2</sub>) The British Drug Houses, Ltd.
- Iradiostoleum** (Solution of vitamin A and Iradiostol) The British Drug Houses, Ltd.
- Kalsolac** (Capsules containing calcium and vitamin D) Evans Medical Supplies, Ltd.
- Kharophen** (Acetarsol) Burroughs Wellcome & Co.
- Kharsulphan** (Sulpharsphenamine) Burroughs Wellcome & Co.
- Kina-Redoxon** (Quinine with vitamin C) Roche Products, Ltd.
- Klotogen** (Vitamin K) Abbott Laboratories (England), Ltd.
- Larostidin** (l-Histidine monohydrochloride) Roche Products, Ltd.
- Leucarsone** (p-Carbaminophenylarsonic acid) May & Baker, Ltd.
- Leucotrope** (Dimethylbenzylaniline disulphonate) Brotherton & Co., Ltd.
- Lytensal** (Theobromine and phenobarbitone tablets) May & Baker, Ltd.
- Magsyn** (Magnesium-synergised aspirin) Allen & Hanburys, Ltd.
- Malacrin** (Mepacrine hydrochloride) May & Baker, Ltd.
- Mandecal** (Compound calcium mandelate) The British Drug Houses, Ltd.
- Mandelix** (Ammonium mandelate elixir) The British Drug Houses, Ltd.
- M. and B. 760** (Sulphathiazole) May & Baker, Ltd.
- M. & B. 693** (Sulphapyridine) May & Baker, Ltd.
- Mecryl** (Mepacrine hydrochloride) May & Baker, Ltd.
- Medinal** (Soluble barbitone preparation) British Schering, Ltd.
- Merfenil** (Phenylmercuric nitrate) May & Baker, Ltd.
- Metabevan** (Vitamin A capsules) Evans Medical Supplies, Ltd.
- Methadone** (Amidone analgesic) T. & H. Smith, Ltd.
- Methedrine** (d-Desoxyephedrine hydrochloride) Burroughs Wellcome & Co.
- Multivite** (Pellets containing vitamins A, B<sub>1</sub>, C and D) The British Drug Houses, Ltd.
- Myanesin** ( $\alpha$ : $\beta$ -Dihydroxy- $\gamma$ -(2-methylphenoxy)-propane) The British Drug Houses, Ltd.
- Nab** (Neoarsphenamine) May & Baker, Ltd.
- Nembudeine** (Pentobarbitone with acetophenetidin and codeine) Abbott Laboratories (England), Ltd.
- Nembutal** (Pentobarbitone) Abbott Laboratories (England), Ltd.
- Neo-Epinine** (Adrenaline homologue) Burroughs Wellcome & Co.
- Neokharsivan** (Neoarsphenamine) Burroughs Wellcome & Co.
- Nipacombin** (Compounded sodio-p-hydroxybenzoate esters) Nipa Laboratories, Ltd.
- Nipagin** (Methyl- and/or ethyl-p-hydroxybenzoate) Nipa Laboratories, Ltd.
- Nipasept** (Compounded esters of p-hydroxybenzoic acid) Nipa Laboratories, Ltd.
- Nipasol** (Propyl-p-hydroxy-benzoates) Nipa Laboratories, Ltd.



- Novarsenobillon** (Neoarsphenamine) May & Baker, Ltd.
- Novostab** (Neoarsphenamine, B.P.) Boots Pure Drug Co., Ltd.
- Oladol** (Vitamins A and D) Abbott Laboratories (England), Ltd.
- Omnopon** (Total opium alkaloids preparation) Roche Products, Ltd.
- Opacin** (Sodium tetraiodophenolphthalein) May & Baker, Ltd.
- Opacol** (Sodium tetraiodophenolphthalein compound) May & Baker, Ltd.
- Opoidine** (Opium alkaloids preparation) J. F. Macfarlan & Co.
- Optochin Base** (Ethyl hydrocupreine alkaloid) Howards & Sons, Ltd.
- Optochin Hydrochlor** (Ethyl hydrocuprein (Optochin) hydrochloride B.P.C.) Howards & Sons, Ltd.
- Oralution** (Ethisterone preparation) British Schering, Ltd.
- Orarsan** (Acetaminohydroxyphenylarsonic acid) Boots Pure Drug Co., Ltd.
- Oraviron** (Methyl testosterone preparation) British Schering, Ltd.
- Ostelin** (Preparation of pure crystalline vitamin D) Glaxo Laboratories, Ltd.
- Ostocalcium** (Calcium sodium lactate and phosphate with vitamin D) Glaxo Laboratories, Ltd.
- Ostomalt** (Malt extract with concentrated orange juice, vitamins A and D, calcium glycerophosphate) Glaxo Laboratories, Ltd.
- Paludrine** (Antimalarial) Imperial Chemical (Pharmaceuticals), Ltd.
- Pandigal** (Digitalis lanata gluconites preparations) Herts Pharmaceuticals, Ltd.
- Paramisal** (Para-aminosalicylic acid) Herts Pharmaceuticals, Ltd.
- Pavopin** (Hydrochlorides of total alkaloids of opium) T. & H. Smith, Ltd.
- Pectevan** (Elixir guaiacol and codeine phosphate) Evans Medical Supplies, Ltd.
- Pelamide** (Nicotinamide) Glaxo Laboratories, Ltd.
- Pelonin** (Nicotinic acid) Glaxo Laboratories, Ltd.
- Peneucin** (Penicillin (calcium salt)) Herts Pharmaceuticals, Ltd.
- Penotrane** (Mercury dinaphthylmethane disulphonate) Ward, Blenkinsop & Co., Ltd.
- Planarsan** (Diethylamine acetarsol) May & Baker, Ltd.
- Planocaine** (Procaine hydrochloride) May & Baker, Ltd.
- Planomide** (Sulphathiazole) May & Baker, Ltd.
- Praequine** (Pamaquin) May & Baker, Ltd.
- Prepalin** (Vitamin A in high concentration) Glaxo Laboratories, Ltd.
- Proseptasine** (Benzylaminobenzenesulphonamide) May & Baker, Ltd.
- Proviron** (Androsterone benzoate preparations) British Schering, Ltd.
- Quinacrine** (Mepacrine hydrochloride and methanesulphonate) May & Baker, Ltd.
- Quiniostovarsol** (Quinine acetarsone) May & Baker, Ltd.
- Quinisan** (Quinine bisalicylosalicylate) Howards & Sons, Ltd.
- Regional "D"** (Amethocaine ampoules) Duncan Flockhart & Co., Ltd.
- Rubyl** (Quinine iodobismuthate) May & Baker, Ltd.
- Rutonal** (Phenylmethylmalonylurea) May & Baker, Ltd.
- Rytol** (Universal photographic developer) Burroughs Wellcome & Co.
- Scalol** (Monomethylparamidophenol sulphate) Johnsons of Hendon, Ltd.
- Septanilam** (Para-aminobenzenesulphonamide) Glaxo Laboratories, Ltd.
- Sevicaine** (Procaine hydrochloride solution) Glaxo Laboratories, Ltd.
- Soamin** (Sodium *p*-aminophenylarsonate) Burroughs Wellcome & Co.
- Solantoin** (Sodium diphenylhydantoinate) Glaxo Laboratories, Ltd.
- Solupyridine** (Neutral soluble sulphapyridine derivative) May & Baker, Ltd.
- Soluseptasine** (Disodium *p*-( $\gamma$ -phenyl-propyl-amino) benzene-sulphonamide- $\gamma$ -disulphonate) May & Baker, Ltd.
- Solusulphamide** (Disodium *p*-( $\gamma$ -phenylpropyl-amino)-benzenesulphonamide- $\alpha$ - $\gamma$  disulphonate) May & Baker, Ltd.
- Soluthiazole** (Neutral soluble sulphathiazole derivative) May & Baker, Ltd.
- Somnifaine** (Oral and injectable solution of two barbiturates) Roche Products, Ltd.
- Sonalgin** (Butobarbital-phenacetin and codeine) May & Baker, Ltd.
- Soneryl** (Butylethylmalonylurea) May & Baker, Ltd.
- Soneryl Sodium** (Sodium butobarbital) May & Baker, Ltd.
- Spasmodin** (Benzyl benzoate puriss. medicinal) W. J. Bush & Co., Ltd.
- Stabilarsan** (Arsphenamine diglucoside in isotonic solution) Boots Pure Drug Co., Ltd.
- Stovaine** (Amylocaine hydrochloride) May & Baker, Ltd.
- Stovarsol** (Acetarsone) May & Baker, Ltd.
- Streptocide** (Sulphanilamide) Evans Medical Supplies, Ltd.
- Sulphamezathine** (Sulphadimethyl pyrimidine) Imperial Chemicals (Pharmaceuticals) Ltd.
- Sulpharsan** (Sulpharsphenamine) Evans Medical Supplies, Ltd.
- Sulphatriad** (Triple sulphonamide tablets) May & Baker, Ltd.
- Sulphonapast** (Sulphanilamide paste) The British Drug Houses, Ltd.
- Sulphostab** (Sulpharsphenamine) Boots Pure Drug Co., Ltd.
- Tabellae Sedativae** (Phenobarbitone and codeine tablets) T. & H. Smith, Ltd.
- Thalazole** (Phthalyl sulphathiazole) May & Baker, Ltd.



**Thalistatyl** (Phthalyl sulphathiazole) Herts Pharmaceuticals, Ltd.

**Theoba** (Theobromine and phenobarbitone) Burroughs Wellcome & Co.

**Theogardenal** (Theobromine-phenobarbital) May & Baker, Ltd.

**Theotone** (Theobromine and phenyl barbitone) Allen & Hanburys, Ltd.

**Thiasolufon** (Neutral soluble sulphathiazole derivative) May & Baker, Ltd.

**Thiazamide** (Sulphathiazole) May & Baker, Ltd.

**V.A.M.** (Divinyl ether anæsthetic mixture) May & Baker, Ltd.

**Vaso-Constrictine** (Adrenalin hydrochloride) Duncan Flockhart & Co., Ltd.

**Veramon** (Barbitone-amidopyrine compound) British Schering, Ltd.

**Vinesthene** (Vinyl ether) May & Baker, Ltd.





## APPENDIX III

STATISTICS OF THE EXPORTS AND IMPORTS of the most important of the Materials described in this book for the month of June 1950 (unless otherwise stated).

Commodity (arranged in order of treatment in this book).	Exports.		Imports.	
	Value in million pounds.	Weight in thousand tons.	Value in million pounds.	Weight in thousand tons.
Crude petroleum . . .	..	..	6.5	208 million gallons
Kerosene (retained im- ports) . . .	..	..	1.3	29 million gallons
Motor spirit (retained im- ports) . . .	..	..	7.2	150 million gallons
Diesel and fuel oil (re- tained imports) . . .	..	..	1.1	45 million gallons
Other mineral oil (retained imports) . . .	..	..	2.6	52 million gallons
Total: refined petroleum (retained imports) . . .	..	..	12.2	276 million gallons
Groundnuts . . .	20.572	..	1.5	28
Palm kernels . . .			2.0	41
Other nuts and oil seeds . . .			1.6	42
Coconut oil . . .			0.2	2
Linseed oil . . .			2.4	21
Palm oil . . .			1.7	22
Other vegetable oils . . .	..	..	3.0	24
Animal and fish oils . . .	..	..	0.9	11
Butter, etc. . . . .	0.159	..	11.3	42
Cheese . . . . .			2.7	16
Soap (hard, in bars) . . .			..	..
Soap (toilet) . . . . .			..	..
Other kinds . . . . .			..	..
Essential oils . . . . .			£365,957	472,279 lbs.
Sugar (unrefined) . . .	..	..	6.6	179
Sugar (refined) . . .	2.9	65	..	..
Wood pulp . . . . .	5.387	..	4.8	155
Paper and board . . .	2.4	23	2.4	54
Artificial silk tissues . .	3.3	19.6 million yards	..	..
Spirits . . . . .	2.6	996 thousand proof gals.	0.6	1070 thousand proof gals.
Wine . . . . .	..	..	0.6	483 thousand gallons
Beer . . . . .	£224,251	20,164 bulk barrels	£402,771	84,678 bulk barrels

Commodity (arranged in order of treatment in this book)	Exports.		Imports.	
	Value in million pounds.	Weight in thousand tons.	Value in million pounds.	Weight in thousand tons.
Rubber (crude and syn- thetic) . . . .	0.072	..	3.9 (retained)	23 (retained)
Coal . . . .	4.687	1276	..	..
Coke, etc. . . .	0.294	66	0.024	..
Ammonium sulphate .	0.4	18.6	2.855	..
Sodium salts . . .	0.8	45.5		
Dyestuffs . . . .	0.9	1.0		
Drugs and medicines .	1.9	..		
Paints and colours .	1.2	..		
Ink (printers') . . .	£117,241	7,952 cwt.	..	..
Ink (writing and drawing)	£38,250	32,115 gals.	..	..
Raw cotton . . . .	..	..	12.7 (retained)	40 (retained)
Cotton yarns . . . .	2.0	2.57	..	..
Cotton thread (finished) .	1.0	0.46	..	..
Unbleached cotton piece goods. . . . .	0.5	4.4 million sq. yds.	2.3	30.1 million sq. yds.
Bleached cotton piece goods. . . . .	1.3	13.0 million sq. yds.		
Printed cotton piece goods	3.0	26.4 million sq. yds.		
Dyed " " "	2.3	15.0 million sq. yds.		
Coloured cottons . .	0.6	3.9 million sq. yds.		
Cattle hides . . . .	0.138	..	1.7	8
Sheep and lamb skins .		..	0.7	2
Undressed fur skins (not rabbit skins) . . .		..	0.9	0.195
Leather . . . . .	1.0	0.85	..	..
Leather footwear . .	0.7	46,000 doz. pairs	..	..
Plastics (1950) . . .	£716,144	54,921 cwt.	£391,672	16,910 cwt.
Tobacco (manufactured) .	1.7	3.8 million pounds wt.	..	..
Tobacco (raw) . . .	1.699	3,000 tons	1.565	3,000 tons

Detailed trade in Plastics for 1947, 1948, and 1949.

Imports in tons for first 6 months of year.

Synthetic resins (vinyl)	{ 1947	..	1,173 tons	..	..
	{ 1948	..	807 tons	..	..
	{ 1949	..	603 tons	..	..
Other synthetic resins	{ 1948	..	841 tons	..	..
	{ 1949	..	268 tons	..	..
Moulding powders	{ 1947	..	3,573 tons	..	..
	{ 1948	..	2,457 tons	..	..
	{ 1949	..	1 ton	..	..
Phenolic and Cresylic	{ 1948	..	386 tons	..	..
	{ 1949	..	1,089 tons	..	..
Polystyrene	{ 1948	..	1,268 tons	..	..
	{ 1949	..	489 tons	..	..
Others	{ 1948	..	..	..	..
	{ 1949	..	..	..	..



## Imports of Plastics from Canada and the U.S.A. (Jan.-June).

Canada.		U.S.A.	
1947 .	. 1,948 tons	1947 .	. 4,011 tons
1948 .	. 1,477 tons	1948 .	. 5,555 tons
1949 .	. 1,346 tons	1949 .	. 2,472 tons

## Imports of Plastics from all Countries (Jan.-June).

1947 .	. 6,217 tons.	Value	£2,000,000.
1948 .	. 7,353 tons.	Value	£2,214,000.
1949 .	. 4,167 tons.	Value	£1,731,000.

## Exports of Plastics Materials in tons (Jan.-June).

Solid and liquid synthetic resins and adhesives . . .	{	1947 .	. 2,683 tons.	Value	£400,000.
		1948 .	. 4,045 tons.	Value	£700,000.
		1949 .	. 4,707 tons.	Value	£825,000.
Moulding powders .	{	1947 .	. 2,405 tons.	Value	£390,000.
		1948 .	. 3,377 tons.	Value	£621,000.
		1949 .	. 2,784 tons.	Value	£588,000.
Sheet, rod, tube and film . . .	{	1947 .	. 1,277 tons.	Value	£723,000.
		1948 .	. 1,473 tons.	Value	£807,000.
		1949 .	. 2,297 tons.	Value	£1,119,000.

## Value of Exports of Plastics to various Countries (Jan.-June) in £.

	1947.	1948.	1949.
India . . . . .	£90,647	£52,956	£257,248
Australia . . . . .	208,716	350,511	277,987
Ireland and British Countries .	201,795	266,561	377,993
Sweden . . . . .	130,362	244,834	163,067
Norway . . . . .	77,060	52,861	110,579
Denmark . . . . .	149,471	74,704	173,668
Netherlands . . . . .	105,316	160,441	197,815
Belgium . . . . .	88,371	102,225	98,245
France . . . . .	113,656	228,602	69,170
Switzerland . . . . .	57,193	63,806	34,149
Czechoslovakia . . . . .	46,978	91,424	150,584
Egypt . . . . .	23,692	48,147	43,826
Argentina . . . . .	50,393	57,505	107,440
Others . . . . .	169,365	337,505	470,023
Total . . . . .	<u>£1,513,015</u>	<u>£2,132,082</u>	<u>£2,531,794</u>

## Production and Consumption of Plastics in 1947 in tons.

Plastic.	Production.	Consumption at home.
Phenolics . . . . .	10,970	11,111
Cresylics . . . . .	11,727	11,115
Urea . . . . .	15,487	12,528
Phenolic and cresylic moulding powders .	24,723	26,709
Urea moulding powders . . . . .	7,941	7,248
Cellulose acetate moulding powders . .	3,730	2,863
Cellulose acetate sheet, rod and tube .	1,310	1,195
Cresylic resin moulding powders . . .	4,361	3,484
Celluloid . . . . .	2,091	2,071
Polyvinyl chloride (plasticised) . . .	11,278	10,890
Casein plastics . . . . .	2,528	2,156



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